

การเสริมสมบัติเชิงกลของวัสดุเชิงประกอบพอลิโพรพิลีนและพอลิเอสเตอร์/ไฟ้ายด้วยเครื่องพลาสมาไฟกัส



นายพิษณุ จำปา

สถาบันวิทยบริการ

จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ภาควิชาวัสดุศาสตร์

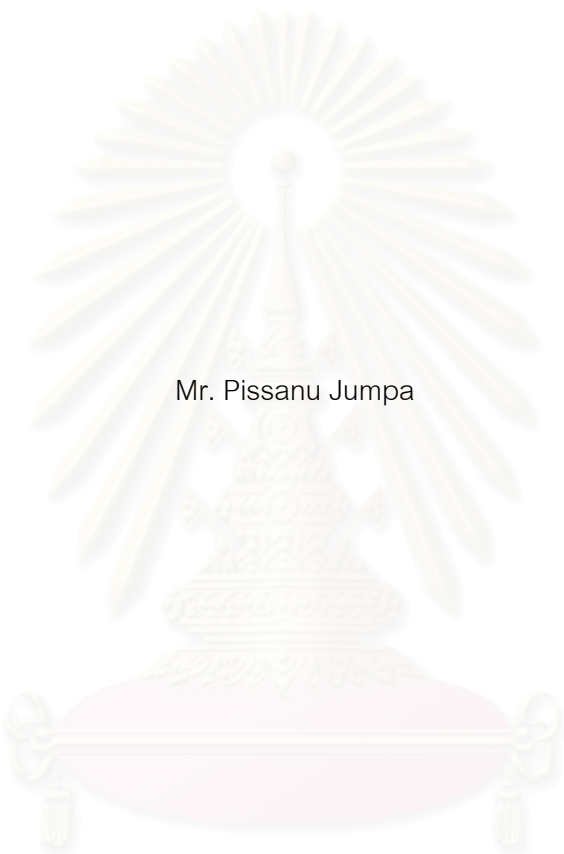
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2548

ISBN 974-14-2071-4

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

MECHANICAL PROPERTY ENHANCEMENT OF POLYPROPYLENE AND POLYESTER/COTTON
COMPOSITES USING A PLASMA FOCUS DEVICE



Mr. Pissanu Jumpa

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Applied Polymer Science and Textile Technology

Department of Materials Science

Faculty of Science

Chulalongkorn University

Academic Year 2005

ISBN 974-14-2071-4

Thesis Title Mechanical Property Enhancement of Polypropylene and Polyester/Cotton Composites Using A Plasma Focus Device

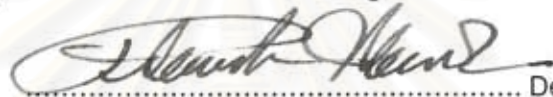
By Mr. Pissanu Jumpa

Field of study Applied Polymer Science and Textile Technology

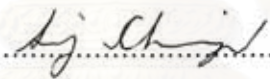
Thesis Advisor Associate Professor Vimolvan Pimpan, Ph.D.

Thesis Co-advisor Assistant Professor Rattachat Mongkolnavin, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master 's Degree



..... Dean of the Faculty of Science
(Professor Piamsak Menasveta, Ph.D)


THESIS COMMITTEE


..... Chairman
(Associate Professor Saowaroj Chuayjuljit)


..... Thesis Advisor
(Associate Professor Vimolvan Pimpan, Ph.D.)


..... Thesis Co-advisor
(Assistant Professor Rattachat Mongkolnavin, Ph.D.)


..... Member
(Associate Professor Paiparn Santisuk)


..... Member
(Associate Professor Werusak Udomkichdecha, Ph.D)

นายพิษณุ จำปา : การเสริมสมบัติเชิงกลของวัสดุเชิงประกอบพอลิโพรพิลีนและพอลิเอสเตอร์/
 ฝ้ายด้วยเครื่องพลาสมาไฟกัส. (MECHANICAL PROPERTY ENHANCEMENT OF
 POLYPROPYLENE AND POLYESTER/COTTON COMPOSITES USING A PLASMA
 FOCUS DEVICE) อ.ที่ปรึกษา : รศ.ดร.วิมลวรรณ พิมพ์พันธุ์, อ.ที่ปรึกษาร่วม : ผศ.ดร.รัฐชาติ
 มงคลนาวิน 105 หน้า. ISBN-974-14-2071-4.

งานวิจัยนี้เสนอแนวทางในการประยุกต์เครื่องพลาสมาไฟกัสแบบ UNU/ICTP ในการเสริมสมบัติ
 เชิงกลของวัสดุเชิงประกอบ โดยนำอนุพลาสมาพอลิโพรพิลีนมาตัดแปรผิวด้วยเครื่องพลาสมาไฟกัสขนาด
 3 กิโลจูลส์ ซึ่งทำงานภายใต้บรรยากาศของแก๊สไนโตรเจนหรือออกซิเจน ที่ความดัน 1.5 มิลลิบาร์ และ
 จำนวนครั้งของการยิงพลาสมา 4 ครั้ง จากการวิเคราะห์ค่ามุมสัมผัสของน้ำพบว่า อนุพลาสมาพอลิโพรพิลีน
 ที่ตัดแปรผิวด้วยพลาสมามีสมบัติชอบน้ำเพิ่มขึ้น อันเนื่องมาจากการเกิดหมู่ฟังก์ชันที่ชอบน้ำขึ้นบนผิวผ้า
 ซึ่งสามารถยืนยันได้ด้วยเทคนิคเอทีอาร์-เอฟทีไออาร์สเปกโทรสโกปี เมื่อนำอนุพลาสมาพอลิโพรพิลีนกับ
 อนุพลาสมา พอลิเอสเตอร์และฝ้าย ในอัตราส่วนโดยน้ำหนักเป็น 80:20 มาลามิเนตด้วยกระบวนการอัดแบบ
 ณ อุณหภูมิ 190 องศาเซลเซียส เป็นเวลา 12 นาที ได้วัสดุเชิงประกอบพอลิโพรพิลีน-พอลิเอสเตอร์/ฝ้าย
 จากการศึกษาพบว่า ความทนแรงกระแทกของวัสดุเชิงประกอบที่ผ่านการตัดแปรผิวทั้งหมดมีค่าเพิ่มขึ้น
 อย่างมาก เมื่อเปรียบเทียบกับของวัสดุเชิงประกอบที่ไม่ผ่านการตัดแปรและพลาสมาพอลิโพรพิลีน
 ในขณะที่สมบัติด้านแรงดึงและด้านแรงดัดโค้งมีค่าใกล้เคียงกัน นอกจากนี้ ยังพบว่า ชนิดของแก๊สและ
 ตำแหน่งการตัดแปรอนุพลาสมาพอลิโพรพิลีนในแชมเบอร์มีผลต่อสมบัติเชิงกลของวัสดุเชิงประกอบที่ได้
 โดยผลการทดลองทั้งหมดบ่งชี้ว่า วัสดุเชิงประกอบที่เตรียมจากอนุพลาสมาพอลิโพรพิลีนซึ่งตัดแปรผิวด้วย
 พลาสมาออกซิเจนมีสมบัติเชิงกลดีที่สุด เมื่อวางอนุพลาสมาพอลิโพรพิลีน ณ ตำแหน่งด้านบนให้ตรงกับ
 ตำแหน่งของการไฟกัส

สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชาวัสดุศาสตร์

สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ

ปีการศึกษา 2548

ลายมือชื่อนิสิต..... *พิษณุ จำปา*

ลายมือชื่ออาจารย์ที่ปรึกษา..... *วิมลวรรณ พิมพ์พันธุ์*

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..... *[ลายมือ]*

4772408023 : MAJOR APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY

KEY WORD: PLASMA / PLASMA FOCUS / COMPOSITE / ADHESION / MODIFICATION

PISSANU JUMPA: MECHANICAL PROPERTY ENHANCEMENT OF POLYPROPYLENE AND POLYESTER/COTTON COMPOSITES USING A PLASMA FOCUS DEVICE.

THESIS ADVISOR: ASSOC.PROF.VIMOLVAN PIMPAN, Ph.D. THESIS COADVISOR:

ASST.PROF.RATTACHAT MONGKOLNAVIN, Ph.D. 105 pp ISBN 974-14-2071-4.

An application of a UNU/ICTP Plasma Focus device for enhancing mechanical properties of a composite material is presented. Polypropylene (PP) nonwoven was surface-modified using a small 3 kJ plasma focus device operated with nitrogen or oxygen gases at a pressure of 1.5 mbar and 4 plasma shots. Water contact angle analysis revealed an increase in hydrophilicity of the surface of plasma-modified PP nonwoven due to the formation of hydrophilic groups on fabric surface confirmed by ATR-FTIR spectroscopy. The lamination of PP and polyester/cotton (PET/C) nonwovens at weight ratio of 80:20 was carried out by compression molding at 190°C for 12 minutes to obtain PP-PET/C composite material. It was found that impact strength of all surface-modified composites greatly increased when compared to those of unmodified composite and PP plastic while their tensile and flexural properties were comparable. It was also found that the type of gas and the treatment position of PP nonwoven in the chamber affected the mechanical properties of the composites. Overall results indicated that the composite prepared from PP nonwoven surface-modified by oxygen plasma had the best mechanical properties, when PP nonwoven was placed directly on top of the focusing position.

Department Materials Science

Field of study Applied Polymer Science and Textile Technology

Academic year 2005

Student's signature..... *Pissanu Jumpa*.....

Advisor's signature..... *Vimolvan Pimpan*.....

Co-advisor's signature..... *R. Mongkolnavin*.....

ACKNOWLEDGEMENTS

The author would like to express his deep gratitude to his thesis advisor, Associate Professor Dr. Vimolvan Pimpan, and thesis coadvisor, Assistant Professor Dr. Rattachat Mongkolnavin for their kindly reviewing this manuscript, moreover, for their motivation, understanding, and chances giving to the author. Without them, this research could not be completed.

The author also would like to extend his respectfully gratitude to Associate Professor Saowaroj Chuayjuljit, Associate Professor Paiparn Santisuk, and Associate Professor Dr. Werasak Udomkichdecha for their kindly participation as thesis committee and for their valuable comments, suggestions and time to read this thesis.

The author also grateful to Mr. Dusit Ngamrunroj and Mr. Pairud Kamsing for their help in operation of plasma focus device.

The author sincerely thank to Mölnlycke Health Care (Thailand) Limited for providing polypropylene nonwoven and polyester/cotton nonwoven.

The author also sincerely thank to Asian African Association for Plasma Training (AAATP) for supporting UNU/ICTP Plasma Focus Device.

Thanks go towards staffs at Scientific and Technological Research Equipment Center (STREC) and Petroleum and Petrochemical College for their assistance in SEM and ATR/FT-IR, respectively.

Special thanks to all his friends and everyone whose names are not mentioned here for their friendship, love, assistance, motivation and also inspiration. These are much valuable and meant a lot to him.

Finally, and the most of all, the author would like to express his appreciation to his family for their unconditionally love, moral support and understanding in the author self. His family impresses in his mind always and forever.

CONTENTS

	Page
ABSTRACT (THAI).....	iv
ABSTRACT (ENGLISH).....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	x
LIST OF FIGURES.....	xi
CHAPTER I INTRODUCTION.....	1
CHAPTER II LITERATURE SURVEY.....	3
2.1 Composite Materials.....	3
2.1.1 Polymer Matrix.....	3
2.1.1.1 Polypropylene.....	5
2.1.2 Reinforcing Filler.....	6
2.1.2.1 Polyester Fiber.....	12
2.1.2.2 Cotton.....	16
2.1.3 Type of Composites.....	20
2.1.3.1 Particle-reinforced Composites.....	20
2.1.3.2 Fiber-reinforced Composites.....	20
2.1.3.3 Structural Composites.....	22
2.1.4 Literature Survey on Polypropylene Composites.....	23
2.2 Surface Modification of Polymers.....	25
2.2.1 Surface Modification by Chemical Methods.....	25
2.2.2 Surface Modification by Physical Methods.....	29
2.2.2.1 The Effect of Plasma on Substrate Properties.....	32
2.2.2.2 Etching effect of Plasma on Substrate Surface.....	32
2.2.2.3 Activation on Substrate Surface.....	33

	Page
2.2.2.4 Cross-link Formation.....	34
2.2.3 Plasma Focus.....	34
2.2.4 Literature Survey on Surface Modification of Polymers by Plasma Treatment.....	36
CHAPTER III EXPERIMENTAL.....	39
3.1 Materials.....	39
3.1.1 Polypropylene (PP) Nonwoven.....	39
3.1.2 Polyester/Cotton (PET/C) Nonwoven.....	39
3.2 Machines and Equipments.....	40
3.3 Methodology.....	41
3.3.1 Surface Modification of Polypropylene Nonwovens.....	42
3.3.2 Characterization of Surface-modified and Unmodified Polypropylene Nonwovens.....	43
3.3.2.1 Morphological Analysis.....	43
3.3.2.2 Contact Angle Measurement.....	44
3.3.2.3 Chemical Structural Analysis.....	44
3.3.3 Preparation of Polypropylene-Polyester/Cotton Composites.....	45
3.3.4 Mechanical Testing of Polypropylene-Polyester/Cotton Composites.....	46
3.3.4.1 Tensile Properties.....	46
3.3.4.2 Flexural Properties.....	48
3.3.4.3 Impact Strength.....	49
CHAPTER IV RESULTS AND DISCUSSION.....	51
4.1 Characteristics of Surface-modified and Unmodified Polypropylene Nonwovens.....	51
4.1.1 Morphology.....	51
4.1.2 Water Contact Angle.....	54
4.1.3 Chemical Structure.....	55

4.2 Mechanical Properties of Polypropylene-Polyester/Cotton Composites.....	60
4.2.1 Impact Strength.....	61
4.2.2 Tensile Properties.....	62
4.2.3 Flexural properties.....	66
CHAPTER V CONCLUSIONS AND RECOMMENDATIONS.....	70
5.1 Conclusions.....	70
5.2 Recommendations.....	71
REFERENCES.....	73
APPENDICES.....	77
Appendix A.....	78
Appendix B.....	95
BIOGRAPHY.....	105



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

Table	Page
2.1 Mechanical properties of natural fibers and glass fiber.....	12
2.2 Chemical treatments used for modification of natural fibers.....	27
4.1 Water contact angles of unmodified, oxygen plasma-modified and nitrogen plasma-modified PP nonwovens.....	54



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

Figure	Page
2.1 Tacticity of polypropylene.....	6
2.2 Classification of filler particles.....	9
2.3 Chemical structure of Kevlar.....	11
2.4 Chemical structure of poly(ethylene terephthalate).....	13
2.5 Synthesis of 1,4-bis(2-hydroxyethyl terephthalate).....	14
2.6 Synthesis of poly(ethylene terephthalate).....	14
2.7 Morphological structure of cotton fiber.....	17
2.8 Molecular structure and configuration of cellulose.....	17
2.9 Cross-section of cotton fiber.....	18
2.10 (a) Cross-section and (b) longitudinal section of cotton fiber.....	19
2.11 Examples of particle-reinforced composites.....	20
2.12 Fiber orientations in fiber-reinforced composites.....	21
2.13 Structural composites.....	22
2.14 Summary of the active species present in an oxygen plasma.....	31
2.15 Diagrams showing four phases of plasma focus formation.....	36
3.1 Polypropylene nonwoven.....	39
3.2 Polyester/cotton nonwoven.....	39
3.3 Flow chart of experimental procedure.....	41
3.4 UNU/ICTP plasma focus device.....	42
3.5 Sample positions in the chamber of UNU/ICTP plasma focus device.....	43
3.6 A Jeol JSM-6400 scanning electron microscope.....	43
3.7 Cam-plus Tantac contact angle meter.....	44
3.8 Thermo Nicolet Nexus 670 spectrophotometer.....	45
3.9 Configuration of nonwoven placement.....	46
3.10 Compression molding machine.....	46
3.11 A LLOYD Universal testing machine model LR 100K.....	47
3.12 Schematic of tensile test specimen (type IV).....	47

LIST OF FIGURES

xii

Figure	Page
3.13 A LLOYD Universal testing machine model 500.....	48
3.14 Schematic of flexural test specimen.....	49
3.15 A Gotech GP-7045 MD Pendulum impact tester (Izod-type).....	49
3.16 Schematic of Izod-type test specimen.....	50
4.1 SEM images of unmodified PP nonwoven (a), oxygen plasma-modified PP nonwovens: cover position (b), position 1 (c), position 2 (d), and position 3 (e).....	52
4.2 SEM images of unmodified PP nonwoven (a), nitrogen plasma-modified PP nonwovens: cover position (b), position 1 (c), position 2 (d), and position 3 (e).....	53
4.3 ATR-FTIR spectra of unmodified PP nonwoven (a) and oxygen plasma-modified PP nonwovens: cover position (b), position 1 (c), position 2 (d) and position 3 (e).....	56
4.4 Proposed mechanism of oxygen plasma treatment on PP nonwoven.....	57
4.5 Proposed mechanism of nitrogen plasma treatment on PP nonwoven	58
4.6 ATR-FTIR spectra of unmodified PP nonwoven (a) and nitrogen plasma-modified PP nonwovens: cover position (b), position 1 (c), position 2 (d) and position 3 (e).....	59
4.7 Impact strength of polypropylene and polypropylene-polyester/cotton composites.....	61
4.8 Tensile strength of polypropylene and polypropylene-polyester/cotton composites.....	62
4.9 %Elongation at maximum load of polypropylene and polypropylene- polyester/cottoncomposites.....	64
4.10 Young's modulus of polypropylene and polypropylene- polyester/cotton composites.....	65
4.11 Flexural strength of polypropylene and polypropylene- polyester/cotton composites.....	66

Figure	Page
4.12 Deformation at maximum load of polypropylene and polypropylene-polyester/cotton composites.....	67
4.13 Flexural modulus of polypropylene and polypropylene-polyester/cotton composites.....	68



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER I

INTRODUCTION

In composites, the reinforcing fibers sustain almost the entire applied tensile load whereas the role of the matrix is to adhere to the fibers, protect the fibers, and transfer the load through the interface. The mechanical behavior of fiber-reinforced composites is dependent on the statistical fiber strength and the properties of the fiber/matrix interface. For these materials, two fracture modes are currently observed: (1) the interlaminar and intralaminar fractures caused by delamination of the fiber/matrix ply; and (2) longitudinal rupture along the fiber orientation or debonding between fiber and matrix due to the poor interfacial adhesion. Considerable effort has been expended to predict the fracture behavior and to model these materials when load is applied in fiber directions.

Improving the interfacial bonding between reinforcement fibers and polymer matrices can be based on three fundamental adhesion mechanisms thereof: (1) mechanical interlocking, (2) acid–base interaction, or (3) chemical bond formation through reactive intermediates. Therefore, surface modification of the matrix or the reinforcing fiber before incorporation in a composite is necessary in order to improve the fiber-matrix adhesion and consequently, enhance the mechanical properties of that composite.

Plasma is loosely defined as a partially or wholly ionized gas with a roughly equal number of positively and negatively charged particles. It has been dubbed the “fourth state” of matter because of its properties that are similar to those of the gas and liquid. Plasma surface treatment is known as a powerful process used to modify surface characteristics of both metallic and polymeric materials. Plasma can interact with the surface of a material resulting in chemical and physical changes at its surface. These changes include etching, implantation of atom, and radical formation. Plasma can be divided into two types: cold plasma and hot plasma. Previous researches generally have emphasized on using cold plasma generated from several devices for surface modification of the polymers. Since the plasma producing processes of these devices normally continuous and difficult to control, it is often that the polymers are overexposed and this results in polymer degradation.

In this research, UNU/ICTP plasma focus device was used for surface modification of polypropylene nonwoven fabric prior to fabrication of polyester-cotton/polypropylene composites. The main aim of research is to investigate the effects of modified parameters on the appearance and properties of plasma-modified composites. These parameters included the type of gas and the positions in plasma focus device chamber. In addition, the suitable condition for plasma treatment of polypropylene nonwoven was also investigated.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER II

THEORY AND LITERATURE SURVEY

2.1 Composite Materials

Composite material can be defined as a complex solid material consisting of two constituent materials, generally divided as a continuous phase called a matrix and a discontinuous phase called reinforcing filler [1]. Generally, a composite material is composed of reinforcement (fiber, particles, flakes, and/or fillers) embedded in a matrix (polymers, metals, or ceramics). The matrix holds the reinforcement to form the desired shape while the reinforcement improves the overall mechanical properties of the matrix. When designed properly, the new combined materials better strength than would each individual material [2].

The roles of the matrix in a fiber-reinforced composite are (1) to transfer stress between the fibers, (2) to provide a barrier against an adverse environmental, and (3) to protect the surface of the fibers from mechanical abrasion. The matrix plays a minor role in the tensile load-carrying capacity of a composite structure. However, a selection of a matrix has a major influence on the interlaminar shear as well as in-plane shear properties of the composite material. Adding a strong interface bond between the fiber and the matrix is obviously desirable, so the matrix must be capable of developing a mechanical or chemical bond to bond the fiber. In addition, these two components should also be chemically compatible, so that undesirable reactions do not take place at the interface [3].

2.1.1 Polymer Matrix

Widely used matrix materials for composites are polymeric materials. For example, in fiber-reinforced composites, the purpose of using a polymer as a matrix is to hold the fibers together so that mechanical loads can be transferred from the weak matrix to the strong fibers. In addition, polymer matrix protects the fibers from handling damages and environmental degradation and, in many cases, contributes some properties such as ductility, toughness,

or electrical insulation. Service temperature is often the main consideration in the selection of a matrix material as well as processing temperature during fabrication [4].

Polymers used as matrices are divided into two broad categories: thermoset and thermoplastic. For thermoset polymer, on the other hand, the molecules are chemically joined together by cross-links, forming a rigid, three-dimensional network structure. Once these cross-links are formed during the polymerization reaction (also called the curing reaction), the thermoset polymer cannot be melted and reshaped (postformed) by the application of heat and pressure. Epoxy and polyester resins have been the most commonly used matrices for several decades, such as in fiberglass-based composites. These thermosetting resins offer a combination of low cost, versatility in many processes, and good property performance.

In the case of thermoplastic polymers, individual molecules are linear in structure with no chemical linking between them. They are held in place by secondary bonds (intermolecular forces) such as Van der Waals forces and hydrogen bonds. With the application of heat and pressure, these intermolecular bonds in a solid thermoplastic polymer can be temporarily broken and the molecules can be moved relative to each other to flow in to new position. Upon cooling, the molecules freeze in their new positions, restoring the secondary bonds between them and resulting in a new solid shape. However, thermoplastics polymer offer many advantages over thermosetting polymers such as flexibility, ease of molding complex parts and ease of processing. Simple methods including extrusion, injection, and compression molding can be used for processing of the thermoplastic-based composites. The forms of materials used can be pellet, bead, film, etc., depending on the processing methods. When natural fibers are used as reinforcing fillers, polyethylene (PE), polypropylene (PP), polystyrene (PS), and poly(vinyl chloride) (PVC) are often used as matrix materials because the processing temperature is restricted to the temperatures below 200°C to avoid thermal degradation of the natural fibers [1, 4, and 5].

In this research, polypropylene was selected to be used as a matrix since the selected reinforcing fillers contained a natural fiber as will be discussed hereafter. General details in its synthesis and properties are given as follows. Polypropylene used was in the

form of nonwoven fabric (PP nonwoven) because of its ease to process by compression molding. However, the information for preparation of PP nonwoven cannot be disclosed due to the policy of the company.

2.1.1.1 Polypropylene

In 1954 G. Natta of Milan following on the work of K. Ziegler in Germany found that certain 'Ziegler-type' catalysts were capable of producing high molecular weight polymers from propylene and many other olefins. By varying the form of catalysts, Natta was able to produce a number of different types of high molecular weight polypropylene which differed extensively in their properties. One type, now known as isotactic polypropylene, was in many ways similar to high density polyethylene but with a higher softening point, rigidity and hardness, the atactic polymer, was amorphous and had little strength.

For the preparation of polypropylene, the C₃ fraction (propylene and propane) is the basic intermediate and this may be separated from the other gases without difficulty by fractional distillation. A typical catalyst system may be prepared by reacting titanium trichloride with aluminium triethyl, aluminium tributyl or aluminium diethyl monochloride in naphtha under nitrogen to form slurry consisting of about 10% catalyst and 90% naphtha. The properties of polymer are strongly dependent on the catalyst composition and its particle shape and size [6].

The regularity or lack of regularity in polymers affects their properties by way of large differences in their abilities to crystallize. Atactic polymers are amorphous (noncrystalline), soft ("tacky") materials with little or no physical strength. The corresponding isotactic and syndiotactic polymers are usually obtained as highly crystalline materials. The ordered structures are capable of packing into a crystal lattice, while the unordered structures are not. Crystallinity leads to high physical strength and increase solvent and chemical resistance as well as differences in other properties that depend on Crystallinity. The prime example of the industrial utility of stereoregular polymers is polypropylene. Isotactic polypropylene is a high-melting, strong, crystalline polymer, which finds large-scale use as both a plastic and fiber. Atactic polypropylene is an amorphous material that find some use

in asphalt blends and formulations for sealants and adhesives but the volumes are very much lower than for isotactic polypropylene [7].

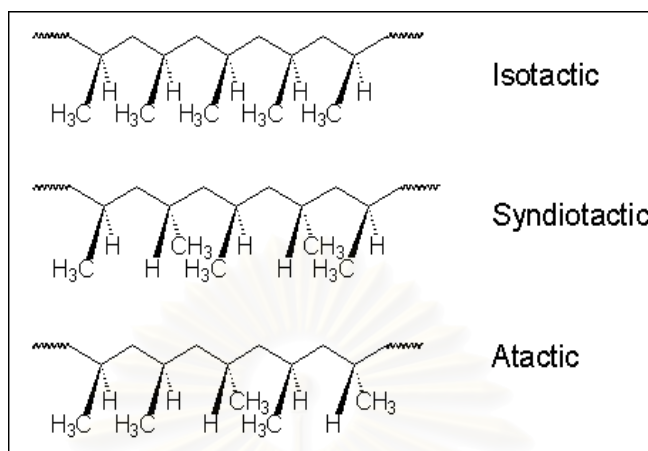


Figure 2.1 Tacticity of polypropylene

Isotactic polypropylene has a lowest density (0.90-0.91 g/cm³) of the major plastics and the processes a very high strength:weight ratio. It has a crystalline melting point of 165-175^oC and is usable to 120^oC; both temperatures are higher than the corresponding values for HDPE. More than 7 billion pounds of polypropylene are produced annually in the united state. About 20% of this volume consists of copolymers, mostly copolymer containing 2-5% ethylene, which imparts increased clarity, toughness, and flexibility. Injection molded products account for about 40% of the total polypropylene volume. This includes durable goods (housing and parts for small and large application, furniture and office equipment, battery, automobile [6, 7].

2.1.2 Reinforcing Filler

Filler can be defined as a solid material capable of changing the physical and chemical properties of materials by surface interaction or its lack thereof and by its own physical characteristics [8]. The extensive uses of the fillers nowadays are mainly for two objectives which are to lower the cost of a molding compound and to selectively modify the properties of a specific plastic. Inert or extender fillers increase the bulk and lower the price while active fillers produce specific improvements in certain mechanical or physical properties and are thus also known as reinforcing fillers [9]. The use of extender fillers can

result in the following changes in the properties of thermoplastics: increase in density; increase in modulus of elasticity, as well as in compressive and flexural strength (stiffening); lower shrinkage; increase in hardness and improvement in surface quality; increase in heat deflection temperature and cost reduction.

Additives for polymer composite have been variously classified as reinforcements, filler or reinforcing filler. Reinforcement, being much stiffer and stronger than the polymer, usually increases modulus and strength. Thus, mechanical properties modification may be considered as their primary function, although their presence may significantly affect thermal expansion, transparency, thermal stability, etc. For composites containing continuous reinforcement, mostly in a thermosetting matrix, the long fibers or ribbons, when pre-arranged in certain geometric patterns may become the major component of the composite (they can constitute as much as 70% by volume in oriented composite). For discontinuous composite, the directional reinforcing agent (short fibers or flakes) are arranged in the composite in different orientations and multiple geometric patterns, which are directed by the selected processing and shaping method. In this case, the content of the additive does not usually exceed 30-40% by volume [10].

Fillers and reinforcements have always played an important role in the plastics industry. The early growth of phenolic plastic industry would not have been possible without the enhancement of properties by the use of fillers and reinforcements. The later commodity resins, such as polyvinyl chloride, polystyrene, polyethylene, and polypropylene, have properties that meet the requirements of high volume end uses; thus they have been sold and used as essentially pure resins. However, recent price escalations, combined with the sporadic and projected shortages of resins and petroleum feed stocks, have established the urgent need for efficient and widespread utilization of fillers and reinforcements. The composite systems afford a means of extending many properties. These improvements in properties are often associated with economic advantages such as lower raw material cost, faster molding cycles as a result of increased thermal conductivity, and fewer rejects due to warpage.

At present, most molded products do not contain any filler or reinforcement, in spite of the fact that the judicious choice of a filler or reinforcement can result in a lower cost product with equivalent or improved properties. Recent technological advances, such as improved dispersion and the often-neglected factor of filler and reinforcement packing, have not been widely applied, and as a consequence, much current information on filled or reinforced plastics indicate poorer properties than the true potential of these composite. Also, there have been recent advances in the equipment and procedures for compounding and molding highly filled polymers. Currently, there are few valid technical justifications for the use of an unfilled resin in most molded products, from a consideration of either properties or moldability. Moreover, as this technology advances, there will be increased benefits from the use of fillers and reinforcements.

A general classification of filler particles is presented in Figure 2.2. The classes are based on a somewhat arbitrary classification according to surface area. This classification is based on two primary properties of fillers; particle size and surface area, both of which are directly measurable and serve as a basis for systematizing filler functions. Most fillers, and those most commonly used, are minerals which are group rock or ores otherwise processed to obtain the material in particulate form. As such, they do not cleave, part, or fracture uniformly and their particles are generally irregular shapes. Certain fabricated fillers, such as glass spheroids, precipitated fillers, and calcium carbonates, will have more nearly precise forms. Kaolinite has the nature of hexagonal platelets, for example, but very rarely will a particle be found that is a true hexagonal platelet [11].

Particle Class Idealized shape class Descriptor ^a	Sphere	Cube	Block (figures for Table 2-1)	Flake	Fiber
	spheroidal ^b	cubic ^c prismatic rhombohedral	tabular prismatic pinacoid irregular	platy flaky ^d	acicular elongated fibrous
Shape ratios:					
length (L)	1	~1	1.4-4	1	1
width (W)	1	~1	1	<1	<1/10
thickness (T)	1	~1	1-<1	$\frac{1}{4}$ -1/100	<1/10
Sedimentation diameter ^e	1	esd	esd	esd ^f	esd ^f
Surface area equivalence ^g	1	1.24 ^h	1.26-1.5 ⁱ	1.5-9.9 ^j	1.87 for 1/10 2.3 for 1/20 ^k
Examples	glass spheres microspheres	calcite ^l feldspar	calcite feldspar silica barite nephelite	kaolin mica talc graphite hydrous alumina	wollastonite tremolite wood flour

Figure 2.2 Classification of filler particles [11]

Another type of widely used fibers is glass fibers. Glass fibers are the most widely used of all reinforcing fillers for plastic matrices. Glass fibers are produced by drawing monofilament of glass from a furnace containing molten glass, coating the monofilament with a polymer to "dull" any surface cracking and gathering a large number of this filament to form a strand of glass fibers [12]. Advantages of glass fibers over other reinforcing fillers include a favorable cost/performance ratio with respect to dimensional stability, corrosion resistance, heat resistance, and ease of processing. The major types of glass fibers are E-glass, S-glass and C-glass. Fiber strength decreases greatly with surface defects and with moisture absorption. The surface of glass fiber can be treated with a size finish or coupling agent to improve the mechanical properties. Glass fibers are mainly used for non-critical applications.

In addition to glass fibers, other types of ceramic fibers used in composites include alumina, boron, silicon carbide, alumina-silica, and other metal oxide-silica fibers. Boron and silicon carbide continuous fibers are made by chemical vapor deposition using other high modulus fibers, such as tungsten and carbon, as the substrates. The high cost of these fibers limited their uses even though they have very high modulus and strength. The other physical properties of these reinforcing fillers in matrices compared with glass fibers and

other fibers are high compressive strength and retention of properties at elevated temperatures.

Mineral fibers such as asbestos although have an excellent high strength and is a low cost reinforcing filler; however, it has been the subject of much legislation, regulation, and litigation in view of the potentially adverse health effects resulting from excess inhalation of free fibers. As a result, material suppliers and fabricators no longer utilize asbestos in composites [13].

Metal fibers including stainless steel, aluminium, and nickel-plated glass or carbon fibers are typically used in composites intended for applications requiring electrostatic charge dissipation or electromagnetic frequency shielding. They are not optimal for reinforcing since they tend to curl up during processing. However, low content of these fibers at about 5-10% is required in order to achieve satisfactory shielding performance but not decrease the mechanical properties of the composites to unacceptable levels. Stainless steel fibers are the most widely used at present.

Besides inorganic fibers mentioned above, organic fibers both synthetic and natural fibers can also be used as reinforcing fillers for composites. The most common organic fibers for composite reinforcing fillers are the aramid and the most common brand name is Kevlar produced by DuPont Corporation.

Aramid fibers are tougher than glass or carbon fibers and are often used in ballistic applications and damage control. The chemical structure of the Kevlar polymeric chain is that of an aromatic polyamide as shown in Figure 2.3

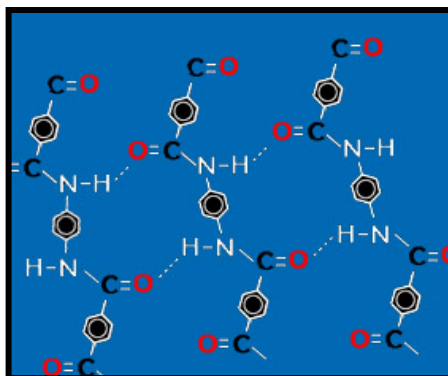


Figure 2.3 Chemical structure of Kevlar

Kevlar aramid is used for high performance composite applications where light weight, high strength, stiffness, impact and fatigue resistance are important.

Polyethylene (PE) fibers, known as Spectra, are produced by solution spinning a high molecular weight PE. Two outstanding features of these fibers are low moisture absorption (1% compare to 5-6% for Kevlar 49) and high abrasion resistance, which make them very useful in marine composites, such as boat hulls and water skis. However, their use at high temperatures (beyond 120°C) is limited due to lose their strength.

Natural fibers are used almost exclusively in low-severity applications for thermoset composites. Some examples are cotton, ramie, jute, flax, sisal and abaca fibers. Of these fibers, jute, ramie, flax and sisal are the most commonly used fibers for polymer composites.

Natural fibers themselves are cellulose fiber-reinforced materials as they consist of microfibrills of cellulose in an amorphous matrix of lignin and hemicellulose. The chemical composition of natural fibers varies depending upon the type of fibers. Primarily, fibers contain cellulose, hemicellulose, pectin and lignin. Hemicellulose is responsible for biodegradation, moisture absorption and thermal degradation of the fibers whereas lignin is thermally stable but is responsible for ultraviolet degradation. Generally, the fibers contain 60-80% cellulose, 5-20% lignin, and up to 20% moisture. The hydrogen bonds and other linkages provide the strength and stiffness to the fibers. The properties of several natural fibers compared to one type of glass fiber are shown in Table 2.1

Table 2.1 Mechanical properties of natural fibers and glass fiber [14].

Fiber	Specific Gravity	Tensile Strength (MPa)	Modulus (GPa)	Specific Modulus (GPa)
Jute	1.3	393	55	38
Sisal	1.3	510	28	22
Flax	1.5	344	27	50
Sunhemp	1.07	389	35	32
Pineapple	1.56	170	62	40
E-glass	2.5	3400	72	28

As can be seen from Table 2.1, the tensile strength and modulus of E-glass fiber are substantially higher than those of natural fibers. But when considering the specific modulus of these fibers (modulus/specific gravity), the natural fibers exhibit this property that is comparable to or better than that of E-glass fiber. The higher specific properties are one of the major benefits of using natural fiber composites for applications where in the desired properties also include weight reduction. Other advantages of using natural fibers are low cost, biodegradable and nonabrasive, unlike other reinforcing fibers. However, they have undesirable properties such as dimensional instability as a result of moisture absorption and low heat resistance, i.e. strength loss sets at around 124°C and thermal degradation commences at around 163°C.

In this research, mixed polyester and cotton fibers in the form of nonwoven fabric (T/C nonwoven) were used as reinforcing fillers. Details in synthesis and properties of each fiber are given as follows. However, the information for preparation of T/C nonwoven cannot be disclosed due to the policy of the company.

2.1.2.1 Polyester Fiber [15]

PET is linear thermoplastic polyester which has widespread commercial use as the major synthetic fiber as well as a film and molding material. The overall volume of PET produced in the USA at the beginning of 1990 was 2.5 million tons of which 1.5 millions tons

was fibers, staple and tows. The repeating unit of PET is the ester of terephthalic acid and ethylene glycol as shown in Figure 2.4.

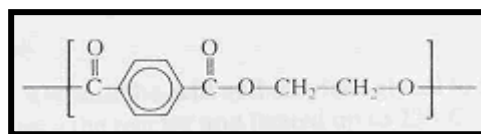


Figure 2.4 Chemical structure of poly(ethylene terephthalate)

PET was first synthesized in 1941 and the commercial production textile fibers started in 1953. At the beginning, the polymer was considered unsuitable for molding as it crystallizes from the melt which makes it brittle. It was not until late 1960s that the polymer was produced in the amorphous state that provided toughness and transparency and enabled PET to be extensively used for blow molded bottles for carbonated soft drinks.

At the beginning, PET was prepared exclusively by the transesterification of dimethyl terephthalate with ethylene glycol and not by the direct acid glycol esterification. The reason for that was the insufficient purity of the acid available at that time. Today the terephthalic acid can be produced with fiber grade purity and both processes, i.e. direct esterification and transesterification, are used commercially for the preparation of the polymer. Terephthalic acid is a white solid that sublimates at 300 °C and is quite insoluble in most common solvent. It is produced by the oxidation of *p*-xylene which is obtained largely from petroleum. Dimethyl terephthalate is also obtained from *p*-xylene by a stepwise process of oxidation and esterification. It melts at 142 °C and is more easily purified than terephthalic acid. From either of the starting materials; the preparation of the polymer is carried out in two steps. In the first step, the so called 'monomer', i.e. bis(2-hydroxyethyl) terephthalate is produced along with some oligomers as shown in Figure 2.5.

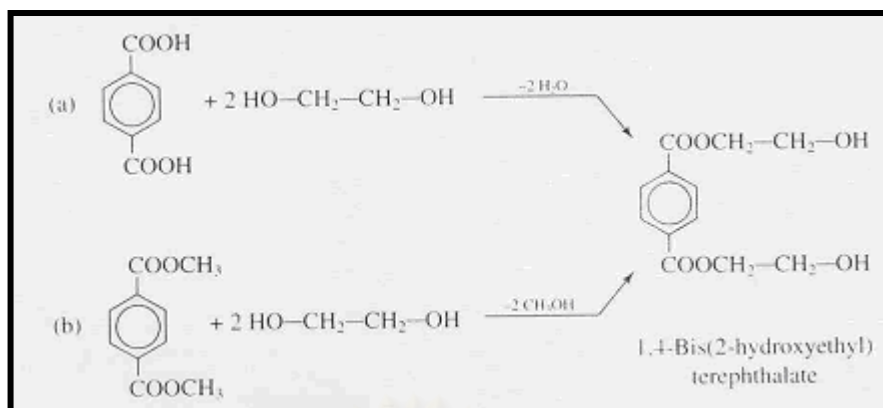


Figure 2.5 Synthesis of 1,4-bis(2-hydroxyethyl terephthalate) [15]

Conditioned terephthalic acid and ethylene glycol in the molar ratio 1:1.5 are introduced into the reactor and heated up to 235 °C. Water from the reaction is eliminated continuously. When dimethyl terephthalate and ethylene glycol are used as starting materials (1:2.2 molar ratio), the transesterification is conducted in the presence of catalysts such as antimony trioxide, cobaltous or manganese acetate. Methanol formed as by-product is removed by the means of a distillation column. Second stage of the process is the same regardless of the starting materials. The bis(2-hydroxyethyl) terephthalate formed in the first stage is condensed in the interchange reaction that occurs in the presence of antimony trioxide catalyst. The pressure is reduced down to 0.13 KPa (1 mm of Hg) in order to eliminate the ethylene glycol liberated in the reaction and to increase the molecular weight as shown in Figure 2.6.

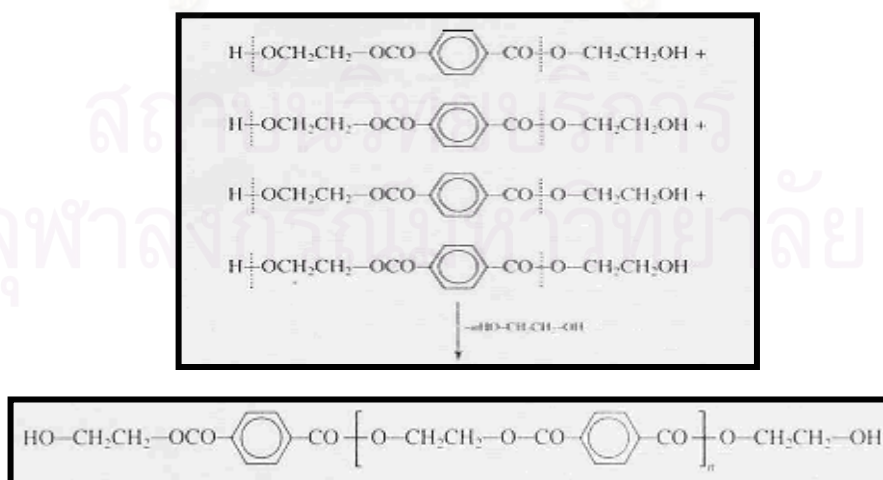


Figure 2.6 Synthesis of poly(ethylene terephthalate) [15]

PET has ability to exist in either an amorphous or a crystalline state. The degree of crystallinity can range from 0 to 60% and is determined by the history of the material. The crystalline melting temperature T_m is 265°C and the glass transition temperature T_g is rather high, being reported about 80°C . When the amorphous polymer is maintained at temperature between T_g and T_m it crystallizes spontaneously. The highest rate of crystallization occurs at $170-180^{\circ}\text{C}$.

These features are very important for the processing conditions of the material. The fiber and film are produced by extrusion and quenching at ambient temperature. Because of their thin section, cooling occurs rapidly and the material remains amorphous and of low resistance. In order to impart good strength, the fiber or film is submitted to a process of hot drawing at a temperature above T_g ($80-100^{\circ}\text{C}$) when orientation and crystallization are induced. The film is biaxially stretched approximately threefold in each direction when the crystallinity is raised to 25%. The tendency to shrink is then reduced by annealing the stretched fiber and the film by heating at 200°C under tension. This treatment increases the crystallinity to 40% and reduces the tendency to shrink on heating. The tensile strength of PET films is 117-173 MPa.

Molded parts can be obtained with amorphous or crystalline structure depending on the temperature of the mold: when the mold is maintained at temperatures below T_g (at around 50°C) and the parts are thin enough to permit a rapid cooling, the material remains amorphous and the moldings are transparent. These parts should not be used above T_g in order to avoid crystallization which leads to shrinkage and clouding. For crystalline and opaque moldings, the polymer is previously compounded with ionomer nucleating agents (substances which induce crystallization) and with plasticizers that decrease T_g . The temperature of the mold is maintained at 130°C to permit the material to rearrange in a crystalline form. Crystalline moldings may be used at temperatures above T_g as they are shape stable up to temperatures near T_m .

A remarkable success on the market was realized with the two liter bottle manufactured for soft drinks where the biaxial stretching from film technology was applied.

In the first step, an amorphous parison is produced by injection into cold mold. Then the parison is heated above the T_g and it possesses high tensile and flexural strength and toughness together with a low permeability to carbon dioxide and oxygen. They allow packing of carbonated beverages under pressures up to approximately 0.4 MPa. Bottles for beer which need an even more reduced permeability to gases have been produced using a multilayer parison from PET and copolymers of vinylidene chloride.

Although the polymer is polar, electrical insulating properties at room temperature even at high frequencies are good because the orientation of the dipoles is restricted below T_g . PET has good resistance to water and dilute mineral acids but is sensitive to base and is degraded by concentrated nitric and sulfuric acids. The resistance to photochemical degradation is very good.

PET can be reinforced with glass fibers up to 55% for injection molded composite products with heat distortion temperatures as high as 220°C . Self-reinforcing PET has been produced by the addition of p-hydroxybenzoic acid which forms liquid crystals in the composite.

A number of copolymers have been prepared in order to lower the T_g value and the tendency to crystallization. They are made by partial replacement of terephthalic acid with isophthalic acid or of ethylene glycol with 1, 4-cyclohexane dimethanol.

2.1.2.2 Cotton

The apparel industry is pre-dominantly cotton based and the share of cotton in total fiber consumption is about 70-75%. Cotton is single cell fiber and develops from the epidermis of the seed. An elongation period continues for 17-25 days after flowering. Cotton consists of cellulosic and non-cellulosic material. A morphological structure of cotton fiber is given in Figure 2.7.

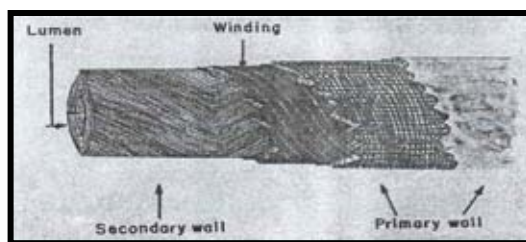


Figure 2.7 Morphological structure of cotton fiber [16].

The outer most layer of the cotton fiber is the cuticle, covered by waxes and pectin, and this surrounds a 'primary wall'. Built of cellulose, pectin, waxes and proteinic material. The inner part of the cotton fiber comprises the 'secondary wall', subdivided into several layer of parallel cellulose fibrils, and the lumen. The smallest unit of the fibrils is the elementary fibrils, consisting of densely packed bundles of cellulose chain, for which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions in a longitudinal direction. Inside the microfibrils, a microcapillary system is developed. These two capillary systems are responsible for swelling and absorption processes which are important for the pre-treatment of cotton. The primary and secondary wall cellulose result form different polymerization mechanisms.

Cotton consists of practically pure cellulose and may be chemically described as poly (1, 4- β -D-anhydroglucopyranose)

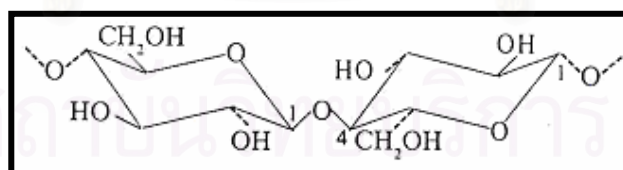


Figure 2.8 Molecular structure and configuration of cellulose [16].

The helical reversal structure of natural cellulose shows the constantly recurring cellobiose unit, consisting of two glucose units each with six carbon atoms. The length of unit cell along the fiber axis is 10.4 Å calculated for the cellobiose unit. In cellulosic fiber, there are 3000-5000 C₆ or glucose units joining together. This corresponds to a molecular weight of the order of 300,000-500,000.

When cotton fiber dry from their initial fully swollen state, the cell wall collapse to give a typical kidney-shaped and the different regions of the cross-section have important differences in structure.

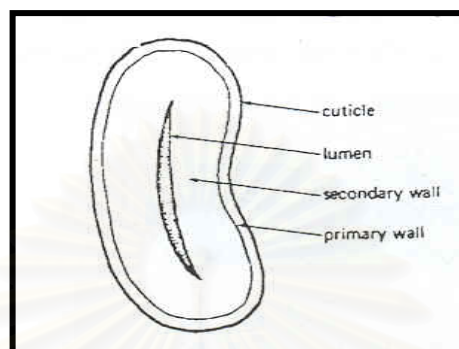


Figure 2.9 Cross-section of cotton fiber [16].

This is commonly referred to as 'bilateral structure' of the cotton fiber. The fiber is more accessible to liquids on the concave side of the fiber. The spiral arrangement of microfibrils reverses direction on rotation periodically along the length of the fiber. Accordingly, some relationships between convolution angle and fiber strength is established.

In the crystalline part, the cellobiose units are closely packed to form Cellulose I in native cellulose fibers and Cellulose II in regenerated cellulose fibers. In Cellulose I the chain molecules are parallel to one another. The folded chain occurs at Cellulose II. In the crystalline regions the chain molecules are antiparallel. Thus, the basis for helical structure for Cellulose I is preferable extended to the structure of Cellulose II [16].

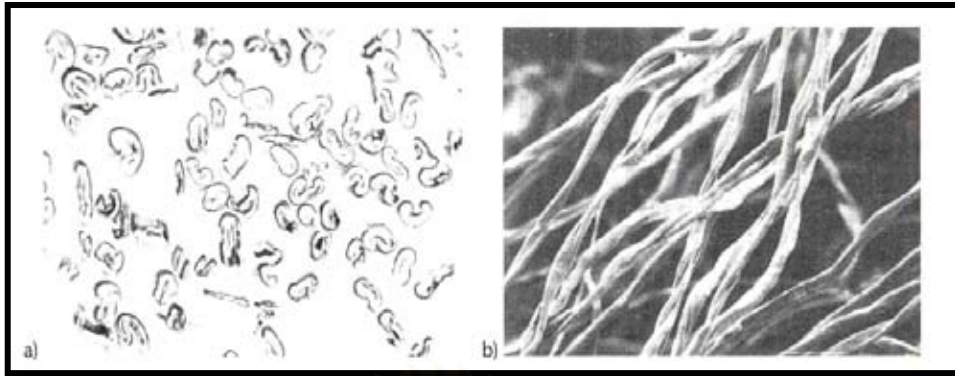


Figure 2.10 (a) Cross-section and (b) longitudinal section of cotton fiber [17]

As shown in Figure 2.10 (a) and (b), cotton shape and structure make it suitable for use for the production of nonwoven bonded fabric: cotton has a ribbon-shaped cross-sectional form, a spiral twist, a hollow structure, a high wet strength for a high module and it is hygroscopic. Thus its use for the production of nonwoven bonded fabrics met with a fair degree of success in the early years. Its success, however, faded quickly because of the impurities which affected the production and even the quality of the finished product. This problem could not be solved, for it is impossible to remove all impurities during the production process or counteract their effect. This technical problem caused the noted decline of cotton usage in the production of nonwoven bonded fabrics.

The composite materials developed thus far have been fabricated to improve mechanical properties such as strength, stiffness, toughness, and high temperature performance. It is natural to study together the composite that have a strengthening mechanism. The strengthening mechanism strongly depends on the geometry of the reinforcement [18]. Therefore, it is quite convenient to classify composite materials on the basis of the reinforcing fillers.

2.1.3 Type of Composites

2.1.3.1 Particle-reinforced Composites

Particles used for reinforcing are ceramics and glasses such as small mineral particles, metal particles such as aluminum, and amorphous materials, including polymers and carbon black. Particles are used to increase the modulus of the matrix, to decrease the permeability of the matrix, to decrease the ductility of the matrix. Particles are also used to produce inexpensive composites. Reinforcing and matrix can be common, inexpensive materials and are easily processed. An example of particle-reinforced composites is an automobile tire which has carbon black particles in a matrix of polyisobutylene elastomeric polymer. Another example is spheroidized steel where cementite is transformed into a spherical shape which improves the machinability of the material. Another example for particle-reinforced composite is concrete where the aggregates (sand and gravel) are the particles and cement is the matrix. Particle reinforced composites support higher tensile, compressive and shear stresses.

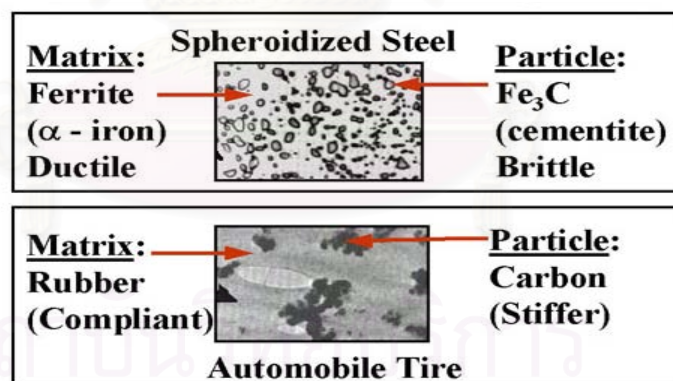


Figure 2.11 Examples of particle-reinforced composites [19]

2.1.3.2 Fiber-reinforced Composites

Reinforcing fibers can be made of metals, ceramics, glasses, or polymers that have been turned into graphite and known as carbon fibers. Fibers increase the modulus of the matrix material. The strong covalent bonds along the fiber's length give them

a very high modulus in this direction. This is because in order to break or extend the fiber, the bonds must also be broken or moved. The stiffness and the strength of composites is dependent upon the mechanical properties of the constituents, but also upon the stress transfer processes occurring at the fiber/matrix interface [20]. Fiber composite manufacturers often rotate the layers of the fibers to avoid directional variations in the modulus [21]. Fibers are difficult to process into composites which makes fiber-reinforced composites relatively expensive. Fiber-reinforced composites are used in some of the most advanced and most expensive sports equipment such as a time-trial racing bicycle frame which consists of carbon fibers in a thermosetting polymer matrix.

The arrangement or orientation of the fibers relative to one another, the fiber concentration, and the distribution all have a significant influence on the strength and other properties of fiber-reinforced composites. Applications involving totally multidirectional applied stresses normally use discontinuous fibers, which are randomly oriented in the matrix material. Consideration of orientation and fiber length for particular composites depends on the level and nature of the applied stress as well as fabrication cost. Production rates for short-fiber composites (both aligned and randomly oriented) are rapid, and intricate shapes can be formed which are not possible with continuous fiber reinforcement.

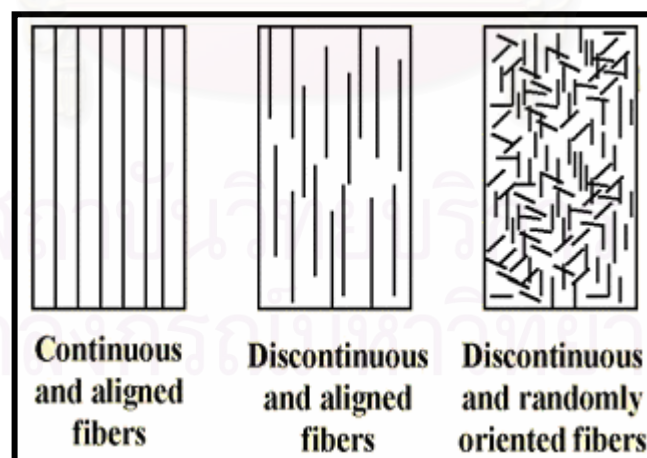


Figure 2.12 Fiber orientations in fiber-reinforced composites [19]

2.1.3.3 Structural Composites

2.1.3.3.1 Laminar Composites

Laminar composite is composed of two-dimensional sheets or panels that have a preferred high strength direction such as found in wood and continuous and aligned fiber-reinforced plastics. The layers are stacked and cemented together such that the orientation of the high-strength direction varies with each successive layer. One example of a relatively complex structure is modern ski and another example is plywood.

2.1.3.3.2 Sandwich Panels Composites

Sandwich panels composite consist of two strong outer sheets which are called face sheets and may be made of aluminum alloys, fiber reinforced plastics, titanium alloys, steel. Face sheets carry most of the loading and stresses. Core may be a honeycomb structure which has less density than the face sheets and resists perpendicular stresses and provides shear rigidity. Sandwich panels can be used in variety of applications which include roofs, floors, walls of buildings and in aircraft, for wings, fuselage and tail plane skins.

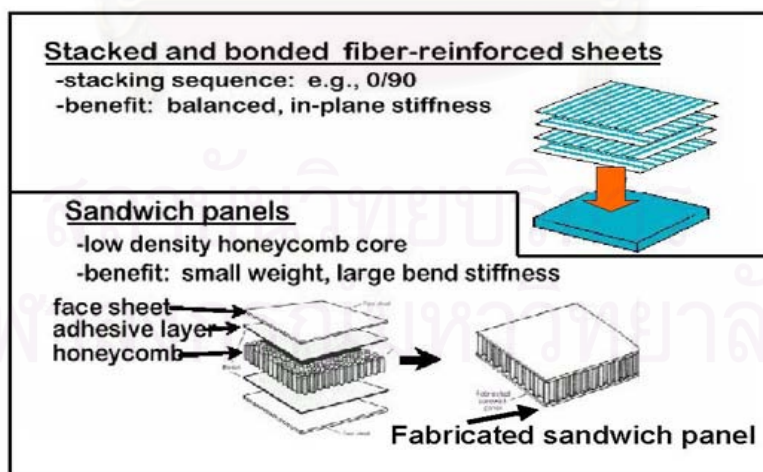


Figure 2.13 Structural composites [19]

2.1.4 Literature Survey on Polypropylene Composites

Studies on composites based on polypropylene matrix and/or cellulose-reinforced have been reported. In 2005 Shibata studied the lightweight laminate composites made from kenaf and polypropylene fibers [22]. In this work, the lightweight laminate composites made from kenaf and polypropylene (PP) fibers were fabricated by press forming. The effects of the number of kenaf layers, heating time and kenaf weight fraction on the flexural modulus of the composite specimen were investigated. The flexural modulus increased with increasing number of kenaf layers and heating time. The increase of the number of kenaf layers contributed to homogeneous PP dispersion in the composite board. This is because more kenaf layers caused better contact between kenaf and PP and prevented PP fibers from shrinking by heating. The increase of heating time contributed to better wetting between kenaf and PP. These observations were revealed with SEM microphotographs. Moreover, the flexural modulus difference between experiment and calculation, which was predicted by Cox's model, increased with decrease of the bulk density and PP weight fraction in the composite board. This was attributed to the decrease of the contact area between kenaf and PP decreasing stress transfer efficiency by kenaf in the lightweight laminate composites. Thus, the optimized kenaf weight fraction, which showed maximum flexural modulus of the composite specimen, decreased with decrease of the bulk density.

Later on 2006 Bullions et al. studied the contributions of feather fibers and various cellulose fibers to the mechanical properties of polypropylene matrix composites [23]. In this work, lightweight laminate composites made from kenaf and polypropylene (PP) fibers were fabricated by press forming. The effects of the number of kenaf layers, heating time and kenaf weight fraction on the flexural modulus of the composite specimen were investigated. The flexural modulus increased with increasing number of kenaf layers and heating time. The increase of the number of kenaf layers contributed to homogeneous PP dispersion in the composite board. This is because more kenaf layers caused better contact between kenaf and PP and prevented PP fibers from shrinking by heating. The increase of heating time contributed to better wetting between kenaf and PP. These observations were revealed with SEM microphotographs. Moreover, the flexural modulus difference between experiment

and calculation, which was predicted by Cox's model, increased with decrease of the bulk density and PP weight fraction in the composite board. This was attributed to the decrease of the contact area between kenaf and PP decreasing stress transfer efficiency by kenaf in the lightweight laminate composites. Thus, the optimized kenaf weight fraction, which showed maximum flexural modulus of the composite specimen, decreased with decrease of the bulk density.

Also in 2006 Arib et al. reported on the mechanical properties of pineapple leaf fiber reinforced polypropylene composites [24]. Pineapple leaf fiber, which is rich in cellulose, relative inexpensive and abundantly available has the potential for polymer-reinforced composite. The present study investigates the tensile and flexural behaviors of pineapple leaf fiber-polypropylene composites as a function of volume fraction. The tensile modulus and tensile strength of the composites were found to be increasing with fiber content in accordance with the rule of mixtures. The tensile modulus and tensile strength with a volume fraction 10.8% are 687.02 and 37.28 MPa, respectively. The flexural modulus gives higher value at 2.7% volume fraction. The flexural strength of the composites containing 5.4% volume fraction was found to be higher than that of pure polypropylene resin by 5.1%. Scanning electron microscopic studies were carried out to understand the fiber-matrix adhesion and fiber breakage.

However, the most important consideration in preparation of a composite is the fiber-matrix adhesion. This process requires a good adhesion between the polymeric matrix and the fibers. Adhesion between the polymer matrix and the fiber has been suggested to be a result of an interaction of two factors: an intimate molecular contact and a maximum attractive force between the components. The concept of intimate molecular contact consists of the following theories: adsorption, diffusion, interlocking, and weak boundary also the maximum attractive force theories involve the theories of chemical bonding, acid-base, electrostatic, and again weak boundary layer. Poor adhesion at the interface means that the full capabilities of the composite cannot be exploited and leaves it vulnerable to environmental attacks that may weaken it, thus reducing its life span. Insufficient adhesion between hydrophobic polymer and hydrophilic fiber results in poor mechanical properties of

the fiber reinforced polymer composites. Therefore, surface modification of the matrix or the reinforcing fibers before incorporation in a composite is necessary in order to improve the fiber-matrix adhesion and consequently, enhance the mechanical properties of that composite. Many reports have shown that surface modification can be done by many methods as presented in the following section.

2.2 Surface Modification of Polymers

The incorporation of a hydrophilic natural fiber in a hydrophobic polymer leads to a heterogeneous system whose properties are inferior owing to lack of adhesion and compatibility between the fiber and the matrix. To achieve compatibility between the two components, surface modifications of these components by either chemical or physical methods can be applied. Chemical methods provide a bridge of chemical bonds between the fiber and the matrix. Physical methods generally change structural and surface characteristics of the fiber and by influencing the mechanical bonding to polymer matrix.

2.2.1 Surface Modification by Chemical Methods

In one general aspect, the invention involves applying a chemical treatment to fibers, such as reinforcing fibers suitable for making a composite article, so as to size and/or preimpregnate the fibers. The chemical treatment has a relatively low viscosity and is substantially solvent-free and non-radiation curable. Heat energy may be employed to lower the viscosity and improve the wetting ability of the applied treatment and/or to increase the molecular weight of, or otherwise cure, the treatment with essentially no generation of solvent vapor [25].

Surface of polymeric materials can be modified by many chemical reactions such as etherification, esterification, etc. For fiber-reinforced composites, chemical modification is usually applied on the reinforcing fibers. Chemical treatments such as delignification, bleaching, acetylation and chemical grafting are generally used for modifying the fiber surface in order to enhance its properties [26].

Delignification is generally carried out by extracting with alcohol or benzene, followed by treating with NaOH and drying at room temperature. Bleaching process results in loss of weight and tensile strength by using many oxidative bleaching agents such as hydrogen peroxide, alkaline calcium or sodium hypochlorite. These losses are mainly attributed to the action of the bleaching agent on the noncellulosic constituents of fiber such as hemicellulose and lignin.

For acetylation process, Khalil et al. studied acetylated plant-fiber-reinforced polyester composites: a study of mechanical, hygrothermal, and aging characteristic [27]. The potential of acetylation of plant fibers to improve the properties of composites was studied. The chemical modification of oil palm empty fruit bunch (EFB), coconut fiber (Coir), oil palm frond (OPF), jute, and flax using noncatalyzed acetic anhydride were investigated. Proof of acetylation was indicated by the increase in weight percent gain (WPG). Acetylation at a reaction temperature of 120°C had resulted in the reduction in the tensile properties (stress, modulus, and elongation at break) of EFB and Coir composites. However, at 100°C, the acetylated samples exhibited improved properties. The mechanical properties of acetylated EFB and Coir-fiber-reinforced polyester composites were evaluated at different fiber loadings. The tensile strength and modulus were improved, but elongation at break was slightly reduced upon acetylation, particularly at high fiber loading. Impact properties were moderately increased for those composites with fiber loadings up to 45%. Acetylation exhibited low moisture absorption, comparable with glass-fiber composites. Acetylated EFB and Coir composites showed superior retention of tensile and impact properties after aging in water up to 12 months.

Chemical grafting involves attaching to the surface of a fiber/filler a suitable polymer with a solubility parameter similar to the polymer matrix. It acts as an interfacial agent and improves the bonding between the fiber and the matrix. Moreover, it can alter the physical and mechanical properties of the composites. Graft copolymerization of vinyl monomers such as methyl methacrylate, acrylamide and acrylonitrile on to cellulose, cellulose derivatives and lignocellulosic fibers has been extensively studied. Impregnation with monomer followed by its polymerization has also been the common method used for

treatment of the fibers. Another method that graft copolymerization onto cellulose takes place through an initiation reaction involving attack by macrocellulosic radicals on the monomer to be grafted. The generation of the macrocellulosic radicals is accomplished by many methods such as diazotization, chain transfer reaction, redox reaction, photochemical initiation and radiation-induced synthesis [26].

The chemical treatment using sodium alginate and sodium hydroxide have been reported for coir, banana and sisal fibers. The treatment resulted in an increase in debonding stress and thus improved the ultimate tensile strength. Table 2.2 lists some examples of chemical treatments used for modification of natural fibers.

Table 2.2 Chemical treatments used for modification of natural fibers [26]

Fiber	Chemical Treatment	Coupling Agent
Wood flour	Succinic acid, styrene, urea-formaldehyde, <i>m</i> -phenylene bismaleimide, acetic anhydride, maleic anhydride, itaconic anhydride, polyisocyanate, linoleic acid, oxalic acid, rosin	Maleated PP, acrylic acid, graft PP, silane, zirconate, titanate
Jute	Phenol-formaldehyde, melamine-formaldehyde, cardanol-formaldehyde	
Sisal	NaOH, isocyanate, sodium alginate, <i>N</i> -substituted methacrylamide	
Pineapple	<i>p</i> -Phenylene diamine	
Banana	Sodium alginate	
Coir	Sodium alginate, sodium carbonate	

Strongly polarized cellulose fibers are incompatible with hydrophobic polymers. When two materials are incompatible, it is often possible to bring intermediate between the

two components. The addition of proper compatibilizer or a coupling agent was another method of the surface treatment that can be used for lowering the interfacial tension and stress transfer across the interface, and promoting the adhesion, dispersion, and compatibilization between the components. Coupling agents are usually (but not limited) used in system of an inorganic filler and organic polymer.

In 1991 Felix et al. studied the nature of adhesion in composites of modified cellulose fibers and polypropylene [28]. In this work, cellulose fibers were surface modified with polypropylene-maleic anhydride copolymer. The physical properties of such fibers were characterized by contact angle measurements, and the chemical structure was identified with ESCA and FTIR. ESCA showed that the modifying agent was localized at the surface of the fibers. The modified fibers were compounded with polypropylene, and composites with various amounts of fibers were manufactured by injection molding. All mechanical properties were improved when treated fibers were used. SEM showed improved dispersion, wetting of fibers, and adhesion. The nature of adhesion was studied using FTIR. It was found that the surface modifying agent is covalently bonded to the fibers through esterification. The degree of esterification is enhanced by activating the modifying agent before fiber treatment. This study has shown the effects of treatment conditions on activation of reactive species and chemical reaction between fiber and modifying agent. Moreover, a better understanding has been achieved of the nature of adhesion for the system.

Later on, in 2005 Arbelaz et al. reported on the mechanical properties of flax fiber/polypropylene composites. Influence of fiber/matrix modification and glass fiber hybridization [29]. The effect of fiber treatments and matrix modification on mechanical properties of flax fiber bundle/polypropylene composites was investigated. Treatments using chemicals such as maleic anhydride, vinyltrimethoxy silane, maleic anhydride-polypropylene copolymer and also fiber alkalization were carried out in order to modify the interfacial bonding between fiber bundles and polymeric matrix. Composites were produced by employing two compounding ways: internal mixing and extrusion. Mechanical behavior of both flax fiber bundle and hybrid glass/flax fiber bundle composites was studied. Fracture

surfaces were investigated by scanning electron microscopy. Results suggest that matrix modification led to better mechanical performance than fiber surface modification. A relevant fact is that silanes or MA grafted onto PP matrix lead to mechanical properties of composites even better than those for MAPP modification, and close to those for glass fiber/PP.

Also in 2005 Doan et al. studied the effect of matrix modification on the properties of jute/polypropylene composites [30]. The investigations of the effect of maleic anhydride grafted polypropylene (MAHgPP) coupling agents on the properties of jute fiber/polypropylene (PP) composites was considered with two kinds of matrices (PP1 and PP2). Both mechanical behaviors of random short fiber composites and micro-mechanical properties of single fiber model composites were examined. Taking into account interfacial properties, a modified rule of mixture (ROM) theory was formulated well and it fit the experimental results. The addition of 2 wt% MAHgPP to polypropylene matrices with significantly improved the adhesion strength with jute fibers and in turn the mechanical properties of composites. It was found that the intrinsic tensile properties of jute fiber were proportional to the fibers cross-sectional area, which was associated with its perfect circle shape, suggesting the jute fibers special statistical tensile properties. The hydrophilic character of natural fibers and, moreover, humidity environmental aging effects were also characterized. The theoretical results were found to coincide fairly well with the experimental data and the major reason of composite tensile strength increase in humidity aging conditions can be attributed to both improved polymer–matrix and interfacial adhesion strength.

2.2.2 Surface Modification by Physical Methods

Polymeric materials can be modified by physical methods such as stretching, calendaring, thermotreatment, and electric discharge such as corona and plasma. The first three methods generally modify not only on the surface but sometimes also the whole structure of the fibers. On the other hand, the implantation process that occurs in plasma treatment is one of the most effective methods for surface modification of polymeric

materials. Gas molecules such as oxygen and nitrogen, are activated by the plasma. The activated species interact with the polymer's surfaces, and then special function, such as hydroxyl, carbonyl, carboxyl, amino groups are formed at the surface of the polymers [31]. As a result, the implantation reactions lead to large changes in the surface properties of the polymer, for example, the polymers change from hydrophobic to hydrophilic.

It is of importance to improve the fiber surface for many applications. Chemical treatment has been traditionally used to modify fiber materials but it has some disadvantages such as influence on bulk properties and environmental pollution. As a type of environmentally friendly physical surface modification technology, plasma treatment can also be used to treat textile materials. Plasma treatment is a simple process without any pollution. Moreover, plasma modification only take place on the uppermost surface of fibers and will not change the bulk properties [32].

Plasma-substrate interaction have been studied for over 30 years, since plasma modification of polymers enhance their surface properties (wettability, adhesion, hydrophobicity, oleophobicity, biocompatibility, permeability, dyeability etc.) without alteration of bulk properties by means of etching/cleaning, polymerization, coating/deposition, etc. instead of using any wet chemical processes. Surface modification is derived by physical and chemical interaction between substrate surface and plasma particles such as ions, atom, ozone, metastables of atomic and molecules, UV-radiation and molecules. Etching is achieved by ion bombardment on substrate surface, leading to surface roughness and weight loss. Fictionalization is achieved by chemical interactions between molecular radicals generated by plasma and active particle in plasma, the UV-radiation generation crosslinking on the subsurface of substrate by recombination of radical [33].

Plasma is loosely defined as a partially or wholly ionized gas with a roughly equal number of positively and negatively charged particles. It has been dubbed the "fourth state" of matter because of its properties that are similar to those of the gas and liquid [34]. Gas phase plasma is an electrically neutral mixture of electrons, ions, radicals, photons,

recombination products and neutrals created by the application of energy, such as radio frequency (RF), to a source gas contained within a vacuum chamber. The Figure.2.14 summarizes the active species that are present in oxygen plasma. Free electrons initiate the process; exposure of the free electrons to the external energy source allows the electrons to gain sufficient kinetic energy, so that a collision with another atom or molecule will result in the formation of ions and radicals. The reactive radical species are capable of chemical work where the ionized atom and molecular species are capable of physical work through sputtering. Photon emission within plasma is a result of the excited neutrals, ions and free radicals formed in the plasma losing their excess energy. The wavelength of the emission is sufficient to break chemical bonds, and can be useful when treating polymeric materials. Though non-equilibrium plasma has electron energies in excess of 10,000°C, critical for sustaining the plasma through atomic and molecular ionization and dissociation processes, it maintains a gas stream temperature that is less than 100°C. The low process temperature is important to products that are temperature sensitive [35].

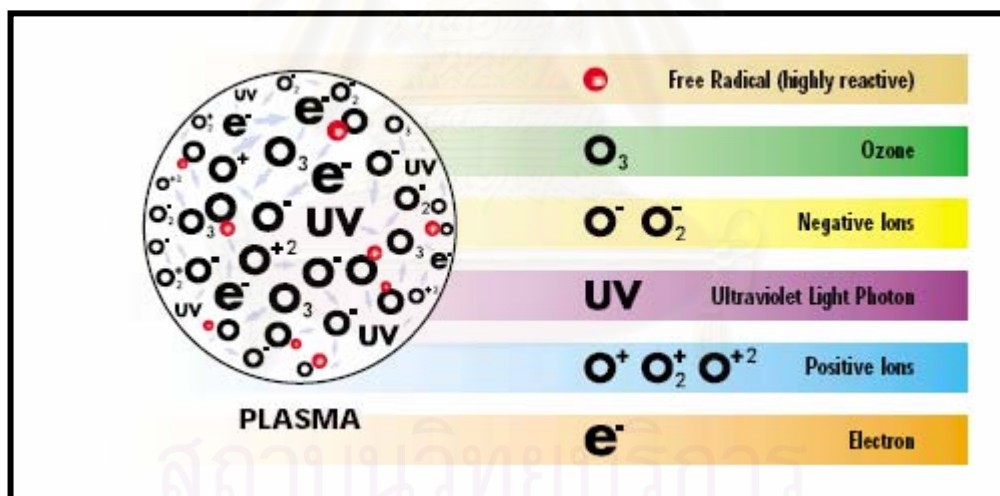


Figure 2.14 Summary of the active species present in an oxygen plasma [35]

Two types of plasma exist - high temperature and low temperature. High temperature plasma is found at atmospheric pressure in its manmade form as a plasma torch such as that used in stainless steel deposition, or occurring naturally as lightning. Low temperature plasmas, used in surface modification and organic cleaning, are ionized gases generated at pressures between 0.1 and 2 torr. Low temperature plasmas work within a

vacuum chamber where atmospheric gases have been evacuated typically below 0.1 torr. These low pressures allow for a relatively long free path of accelerated electrons and ions. Since the ions and neutral particles are at or near ambient temperatures and the long free path of the electrons, which are at high temperature or electron-volt levels, have relatively few collisions with molecules at this pressure the reaction remains at low temperature [32].

2.2.2.1 The Effect of Plasma on Substrate Properties

In plasma bulk, the reactive species (positive and negative ions, neutral species, atoms, metastables and free radicals) are generated by ionization, fragmentation and excitation. And, they lead to chemical and physical interactions between plasma and substrate surface, depending on plasma conditions such as gas, power, pressure, frequency and exposure time. Plasma of Non-polymerizable gases plasmas (Ar, He, O₂, N₂, CO₂, etc.) usually change surface morphology and induce the surface roughness of polymer films. Ions and neutral species in plasma collide with the molecules on the substrate surface, and then etch away physically: that is, etching effect. Consequently, the long molecular chains would be broken into short ones: chain scission. Also, the reactive species lead to chemical interaction with surface molecules, generating new functional groups (functionalization) and radicals. Radicals induce cross-linking generation on the uppermost few mono-layers of polymer. Hydrocarbon and fluorocarbon gases can be used to achieve deposition, and plasma polymerization can be obtained by using monomer gas [32].

2.2.2.2 Etching Effect of Plasma on Substrate Surface

Etching in plasma is a physical removing process of material on the surface of substrate. Etching of surfaces also can be accomplished by plasma. Roughening of the surface can play a significant part in adhesion by increasing the total contact area between the adhesive and the subsurface. Etching is a result of gas selection or the length of time the surface is exposed to the plasma. Ablation can be accomplished with either active or inert gases and can be run to excess causing extremely porous surfaces by too

long of an exposure to the plasma [34]. Etching in plasma treatment has no unfavorable effect on the physical properties of substrate because only few hundred Å layers are etched away. Surface morphology and micro-roughness are achieved by etching process, preferring to 33 removing amorphous region: that is, selective etching. However, the particles etched would be re-deposited on substrate surface again, and provide undesirable results on etching processing. Solid particles can be generated in the plasma when the concentration of particles coming off substrate surface is dense enough to interact with molecules on substrate surface or wall of reactor of plasma system [36].

2.2.2.3 Activation on Substrate Surface

When the substrate is subject to plasma exposure, the plasma species (ions, electrons, radicals, UV-radiation, neutrons, etc.) interact with substrate chemically and physically. Initially, the gas molecules are dissociated into active species such as ions, electrons, and radicals in the plasma chamber. The active species would collide with the molecules on substrate surface [33]. UV-radiation and the collisions lead to the radical formation by chain scission of molecules and abstraction (taking-off of atoms on molecular chain) [35]. Free radicals generated in the plasma treatment on polymeric materials play an important role in surface modification. Radical species on plasma would interact with the radicals on substrate molecules, and then new functional groups are generated, These functional groups modify generally modify the chemical activity of the surface. The new functional groups have strong chemical bonds with the bulk material and have the capability to further bond with adhesives to promote better adhesion. The functional groups also increase the surface area available for the adhesive and thus will distribute the load over a larger area resulting in improved adhesive strength [38].

The stability of free radicals is directed by the nature of the chemical bonds that are broken [38]. Moreover, the chain cross-linking is induced by re-combination between radicals. After plasma treatment on the substrate, unstable free radicals would recombine rapidly with other active species while stable free radicals remain as living radicals [39].

2.2.2.4 Cross-link Formation

It is well known that the radical formation is strongly related to ion bombardment and UV-radiation. Cross-link is due to the interaction between two or more radicals to establish covalent link, the bombardment and the radiation given out by plasma particles causes the breakage of polymer macro-molecules and the current creation of free radical, in this way a cross-linked polymeric layer is rapidly formed [40]. Argon plasma effectively sputters nanometers of material from the sample surface, literally roughening the surface on the nanometer scale, the cross linking that results improves the adhesion of metal layers to the plasma-treated polymer laminate [38].

2.2.3 Plasma Focus

The plasma focus system (PF) was built in early 1960s as a modification of classically Z-pinch by Filipov in Russia and Mather in the USA [41]. A dense plasma focus device is a pulsed coaxial accelerator that produces a high-density, high-temperature plasma along with particle beams and electromagnetic radiation [42]. Whereas the generation of energetic ion beam by the plasma focus has been unambiguously demonstrated, it is realized that the shot to shot variation of the ion beam intensity is very large. More seriously, since the optimum operating pressure for consistent focusing is higher than 0.1 mbar, it makes the utilization of the ion beam for particle application difficult. It is known that the range of nitrogen ion beam in an ambient nitrogen gas of 0.5 mbar is less than 50 cm. On the other hand, a strong plasma jet in the form of blast wave is observed to travel away from the anode, in the same direction as the ion beam [43].

The process of plasma focus begins when a charged capacitor bank at a voltage V_0 discharges to plasma focus tube. The high voltage causes a breakdown, initially, on the surface of the glass insulator at the base of the anode. A current sheath (plasma sheath) is formed symmetrically along the electrode axis. It lifts off from the glass insulator and is then propelled by $\vec{J} \times \vec{B}$ force or usually known as Lorentz force. Here, \vec{J} is the

current density and \vec{B} is the self-induced magnetic field. This phase is called "breakdown or surface discharge" phase as shown in Figure 2.15a.

Next phase starts when the current sheath lift-off is completed and the current flows radially outward from the inner anode to the outer cathodes. As this happens, it builds up a thicker current sheath. When the current sheath is moving out with speed, it will form a shock front in front of the current sheath. The current sheath sweeps up all the charged particles it encountered leaving behind a vacuum immersed in the magnetic field of the current sheath. Between the shock front and the current sheath, the gas is shock heated to a highly ionized state and a plasma slug will be formed. Ahead of the shock front, the ambient gas is assumed to be undisturbed. The $\vec{J} \times \vec{B}$ force pushes the current sheath towards the end of the inner electrode along the Z-direction. This phase is called the "axial acceleration phase" as shown in Figure 2.15b

When the current sheath reaches the end of the anode, the radial phase starts. During the radial phase the current sheath slides along the surface of the anode in the radial direction by the $\vec{J} \times \vec{B}$ force. The current sheath collapses radially. This phase is called "radial collapse phase" as shown in Figure 2.15c. At the end of the radial phase, a dense plasma column is formed on the axis of the focus tube just off the face of the anode. During this dense plasma phase, soft X-ray and other types of radiations can be emitted from the plasma. This final phase is the focusing phase as shown in Figure 2.15d

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

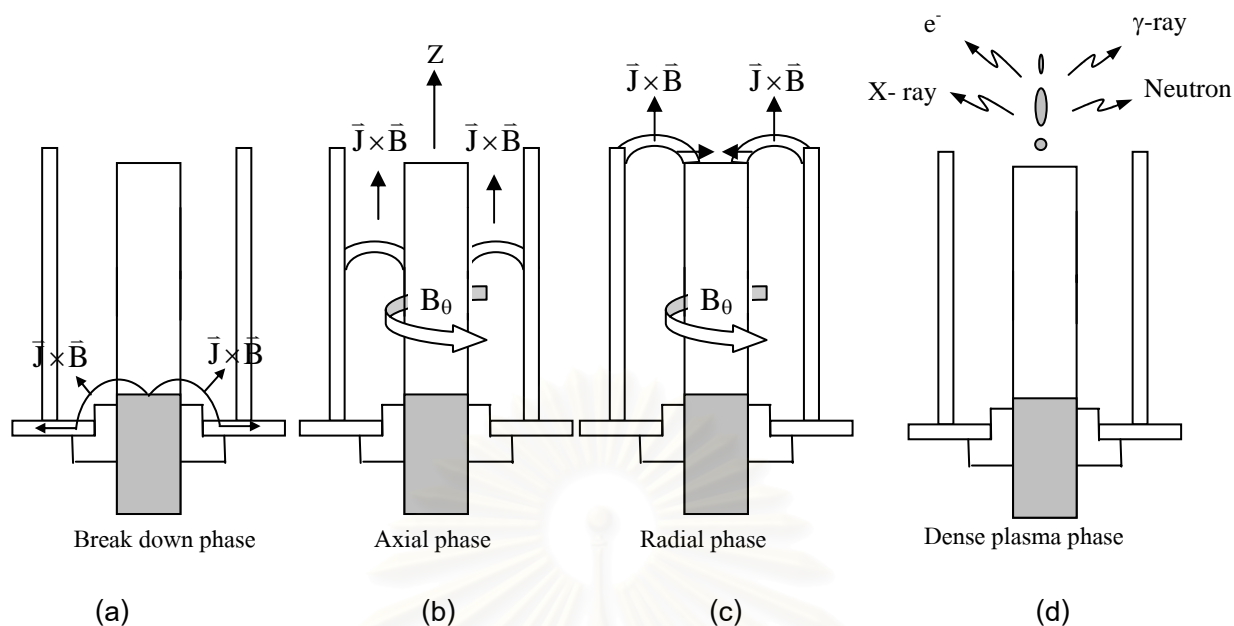


Figure 2.15 Diagrams showing four phases of plasma focus formation [44]

2.2.4 Literature Survey on Surface Modification of Polymers by Plasma Treatment

In 1996 Caiazza et al. studied electrode discharge for plasma surface treatment of polymeric materials [45]. A cold plasma prototype electrode discharge apparatus to perform polymer surface treatment is described. The plasma generator, operating with oxygen and/or nitrogen, works in glow regime at low pressure (10 mbar) and at relatively high gas flow rate, in the 110-340 l/h range. The effects of treatment on PET monopolyester and glass fiber reinforced plastics (GFRP) surface are analyzed. The treatment points out, in all operating conditions, an increase of both wettability (PET) and adhesivity (GFRP). The treatment times obtained are one order of magnitude lower than those of the traditional treatment apparatus.

In 2002 Carino et al. studied the cold plasma treatment of polypropylene surface a study on wettability and adhesion [40]. The present work deals with air cold plasma treatment of polypropylene surfaces. Particularly, the influence of AC electrical discharge cold plasma parameters on wettability and adhesion of polymeric surfaces was studied. Also, the nature of the relationship between wettability and adhesion was investigated.

Owing to the complexity of plasma–work piece interaction, an experimental approach was followed. A set of process variables (voltage, time and air flow rate) was identified and used to conduct some experimental tests on the basis of design of experiment techniques. The experimental results show that the proposed plasma process may considerably increase polypropylene wettability and adhesion properties. These outcomes represent the first step in trying to optimize the polymeric adhesion by means of this non-conventional manufacturing process.

In 2003 Rahel et al. studied the hydrophilization of polypropylene nonwoven fabric using surface barrier discharge [46]. Surface dielectric barrier discharges (SDBD), which find widespread industrial applications in ozone production, were used to hydrophilize light-weight polypropylene nonwoven fabric (PPNF) samples. The samples were treated in nitrogen plasma generated by SDBD at atmospheric pressure. The hydrophilicity of the samples was examined as a function of the storage time using a standard strike-through test. The surface chemical composition was characterized by X-ray photoelectron spectroscopy. Because of very short treatment times obtained (~1 s) and its simplicity the method has the potential to be used in-line with standard high-speed PPNF production lines, laminating, printing and metal plating lines, etc.

In 2004 Wei studied surface characterization of plasma-treated polypropylene fibers [47]. Plasma treatment is increasingly being used for surface modification of different materials in many industries. In this study, different techniques were employed to characterize the surface properties of plasma treated polypropylene fibers. The chemical nature of the fiber surfaces has been investigated by X-ray photoelectron spectroscopy (XPS). The XPS examination indicated the presence of oxygen-containing functional groups on fiber surfaces after plasma treatment. The Atomic Force Microscopy (AFM) scans revealed the evolution of surface morphology under different experimental conditions. A Philips Environmental Scanning Electron Microscopy (ESEM) was also used to study the wetting behavior of the fibers. In the ESEM, relative humidity can be raised to 100% to facilitate the water condensation onto fiber surfaces for wetting observation. The

ESEM observation revealed that the plasma treatment significantly altered the surface wettability of polypropylene fibers.

However, in 2006 Lai et al. studied on hydrophilicity of polymer surfaces improved by plasma treatment [48]. This paper reports on surface properties of polycarbonate (PC), polypropylene (PP), polyethylene terephthalate (PET) samples treated by microwave-induced argon plasma have been studied with contact angle measurement, X-ray photoelectron spectroscopy (XPS) and scanned electron microscopy (SEM). It is found that plasma treatment modified the surfaces both in composition and roughness. Modification of composition makes polymer surfaces tend to be highly hydrophilic, which mainly depended on the increase of ratio of oxygen-containing group as same as other papers reported. And this experiment further revealed that C=O bond is the key factor to the improvement of the hydrophilicity of polymer surfaces. Our SEM observation on PET shown that the roughness of the surface has also been improved in micron scale and it has influence on the surface hydrophilicity.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER III

EXPERIMENT

3.1 Materials

3.1.1 Polypropylene (PP) Nonwoven

Polypropylene (PP) nonwoven was provided by Mölnycke Health Care (Thailand) Limited.



Figure 3.1 Polypropylene nonwoven

3.1.2 Polyester/Cotton (PET/C) Nonwoven

Polyester/cotton (PET/C) nonwoven was provided by Mölnycke Health Care (Thailand) Limited.



Figure 3.2 Polyester/cotton nonwoven

3.2 Machines and Equipments

3.2.1 Plasma Focus Device: UNU/ICTP (United Nation University/International Center for Theoretical Physics)

3.2.2 Compression Molding: Department of Materials Science, Faculty of Science, Chulalongkorn University

3.2.3 Contact Angle Meters: Cam-Plus Tantac.

3.2.4 ATR/FT-IR Testing Machine: Thermo Nicolet Nexus 670

3.2.5 Scanning Electron Microscope (SEM): JSM-6400, Jeol Co, Ltd

3.2.6 Universal Testing Machine: A LLOYD Model LR 100K

3.2.7 Universal Testing Machine: A LLOYD Model 500

3.2.8 Izod-Charpy Pendular Impact Tester: Gotech Testing Machine



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

3.3 Methodology

The flow chart of the entire experimental procedure is shown below in Figure 3.3.

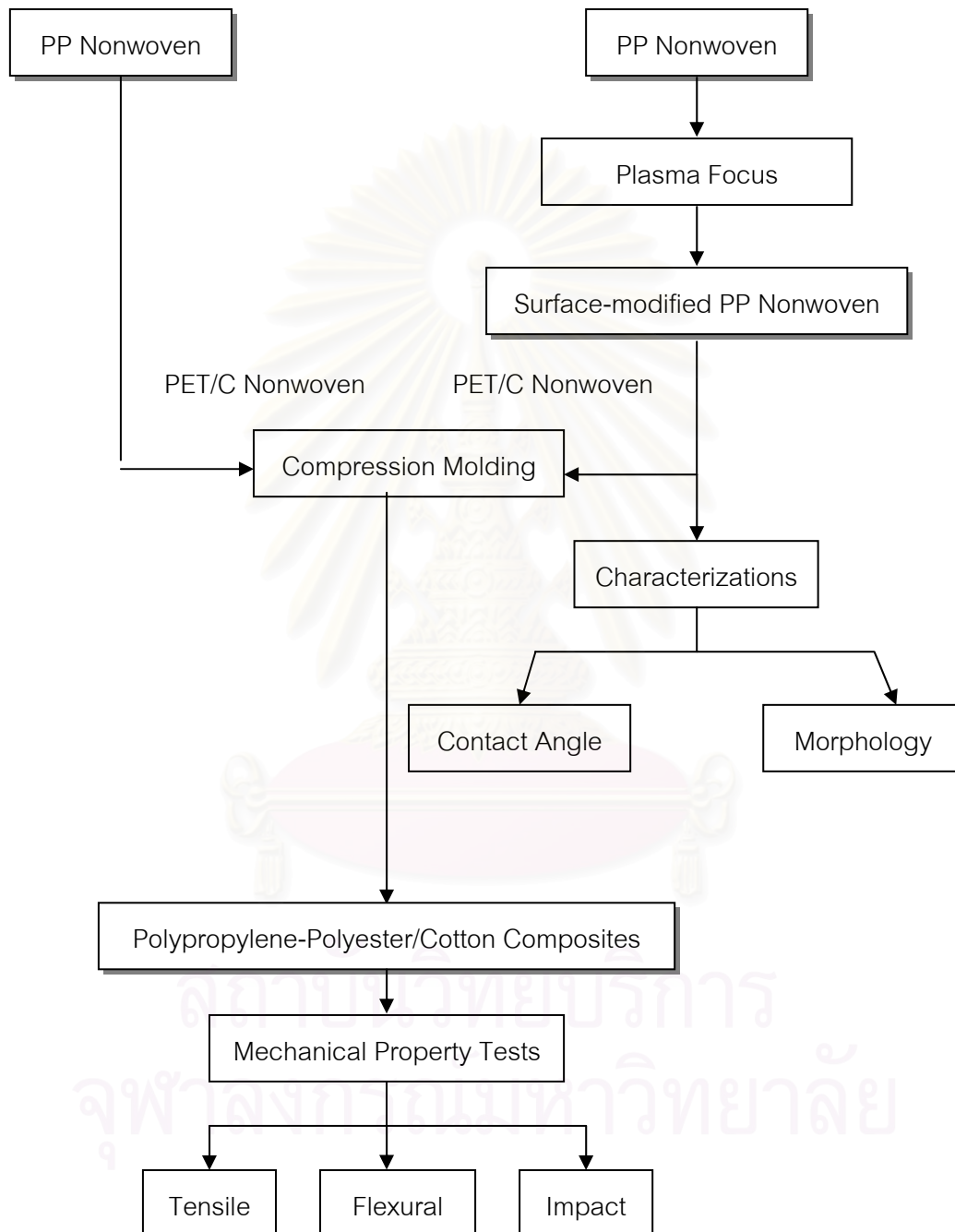


Figure 3.3 Flow chart of experimental procedure

3.3.1 Surface Modification of Polypropylene Nonwoven

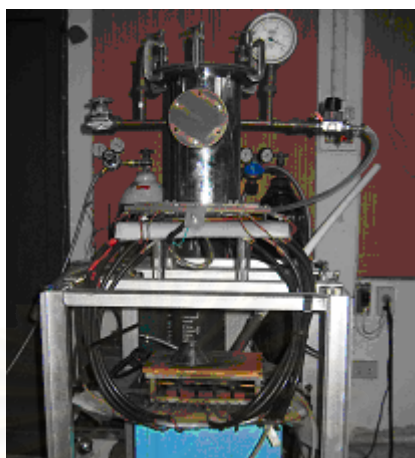


Figure 3.4 UNU/ICTP plasma focus device

Polypropylene nonwoven was surface-modified using UNU/ICTP plasma focus device as shown in Figure 3.4. Four pieces of PP nonwoven having dimensions of 13 cm x 9 cm were placed on the cover and the positions assigned as 1,2,3 respectively in the chamber of UNU/ICTP plasma focus device as shown in Figure 3.5. The plasma focus device was then operated using a selected gas at a pressure of 1.5 mbar and discharge voltage at 12.5 kV. The number of plasma shots used was at 4 shots which was the suitable condition for surface modification of PP nonwoven at the cover position reported by J. Srisawat [49]. After the process completed, PP nonwoven samples were removed from the chamber and subjected to further characterization.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

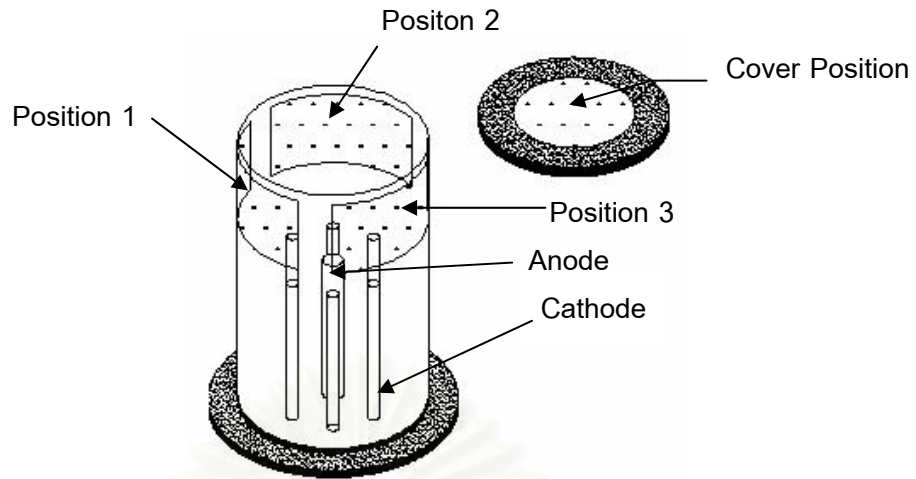


Figure 3.5 Sample positions in the chamber of UNU/ICTP plasma focus device

3.3.2 Characterization of Surface-modified and Unmodified Polypropylene Nonwovens

3.3.2.1 Morphological Analysis

Morphology of surface-modified and unmodified PP nonwovens was verified using Jeol JSM-6400 scanning electron microscope (SEM) as shown in Figure 3.6. The sample was coated with gold before being scanned.



Figure 3.6 A Jeol JSM-6400 scanning electron microscope

3.3.2.2 Contact Angle Measurement

Water contact angles of surface-modified and unmodified PP nonwovens were determined according to ASTM D5725-99 using Cam-Plus Tantac contact angle meter. Five distilled water drops (2 microlite volumes) were randomly dispersed on the surface of PP nonwoven.



Figure 3.7 Cam-Plus Tantac contact angle meter

3.3.2.3 Chemical Structural Analysis

The chemical structures of the samples were analyzed by attenuated total reflection/fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Thermo Nicolet Nexus 670 spectrophotometer as shown in Figure 3.8. The samples were scanned at the frequency range of $4000-600\text{ cm}^{-1}$ with 32 consecutive scans and 4 cm^{-1} resolution.



Figure 3.8 Thermo Nicolet Nexus 670 Spectrophotometer

3.3.3 Preparation of Polypropylene-Polyester/Cotton Composites

As already mentioned, the two components were in the form of nonwoven fabric. The weight ratio of PP nonwoven to PET/C nonwoven was selected to be 80:20. This weight ratio reported by J. Srisawat [49] was the suitable ratio for preparation of the same composite. The configuration of nonwoven placement is shown in Figure 3.9. Each PET/C nonwoven in machine direction was placed in between two modified PP nonwovens. While modified surface was attached to PET/C nonwoven, unmodified surface of these two modified PP nonwovens were adhered to other unmodified PP nonwovens. Before compression using compression molding machine as shown in Figure 3.10, PP and PET/C nonwovens were preheated at 190°C, using a pressure of 500 psi for 5 minutes. Then they were compressed at the same temperature using a pressure of 1000 psi for 7 minutes and PP-PET/C composites were obtained.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

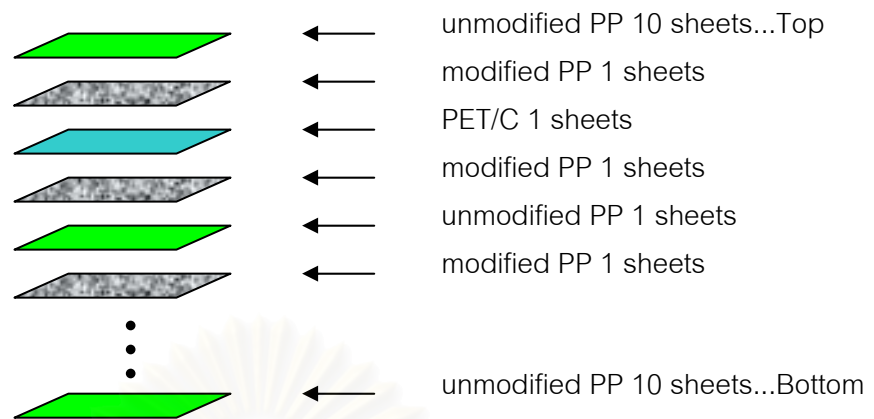


Figure 3.9 Configuration of nonwoven placement



Figure 3.10 Compression molding machine

3.3.4 Mechanical Testing of Polypropylene-Polyester/Cotton Composites

For mechanical testing, it is necessary to note that all specimens of the obtained composites were cut in machine direction of PET/C nonwoven.

3.3.4.1 Tensile Properties

Tensile properties of the composite samples were measured according to ASTM D638-82a (type IV) using a Universal Testing Machine model LR 100K as shown in Figure 3.11.

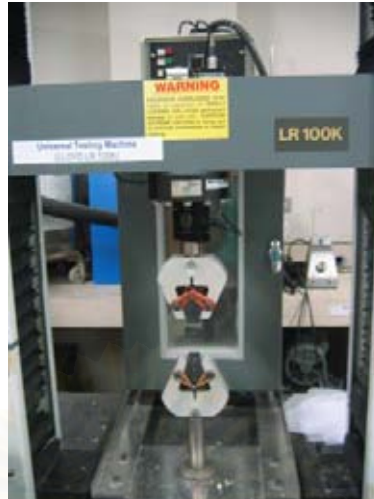
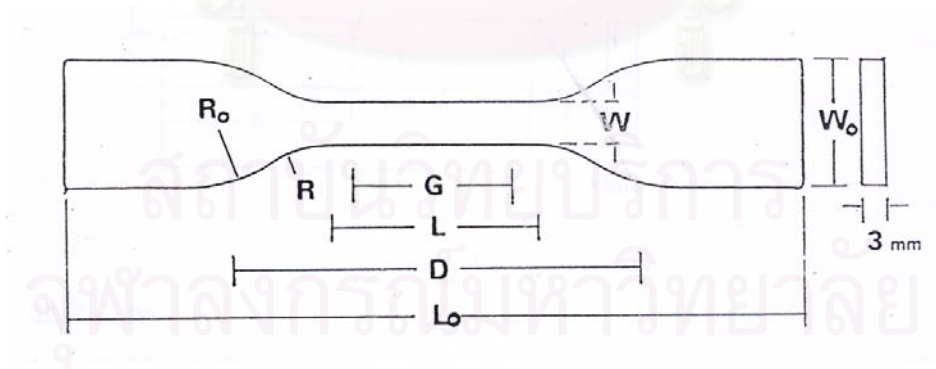


Figure 3.11 A LLOYD Universal testing machine model LR 100K

The tensile testing conditions were as follows:

Temperature: 25°C
 Relative humidity: 50%
 Load cell 1 kN
 Speed of testing: 50 mm/min

The specimens were prepared in a dumbbell shape as shown in Figure 3.12.



W: 6 mm	L: 33 mm	G: 25 mm	R: 14 mm
W ₀ : 19 mm	L ₀ : 115 mm	D: 65 mm	R ₀ : 25 mm

Figure 3.12 Schematic of tensile test specimen (type IV)

3.3.4.2 Flexural Properties

Flexural properties of the composite samples were tested based on ASTM D790-81 using a LLOYD Universal Testing Machine model 500 as shown in Figure 3.13.



Figure 3.13 A LLOYD Universal testing machine model 500

The flexural testing conditions were as follows:

Temperature: 25°C
Relative humidity: 50%
Load cell 2500 kN
Speed of testing: 50 mm/min

The specimen were prepared in a rectangular shape as shows in Figure 3.14.

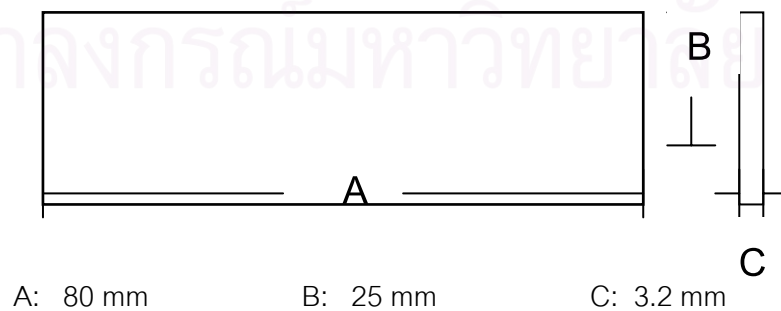


Figure 3.14 Schematic of flexural test specimen

3.3.4.3 Impact Strength

Impact tests of the composites were performed on a Gotech GP-7045MD Testing Maching Izod-Charpy Pendular Impact Tester according to ASTM D256-04 (Izod-type) as shown in figure 3.15.



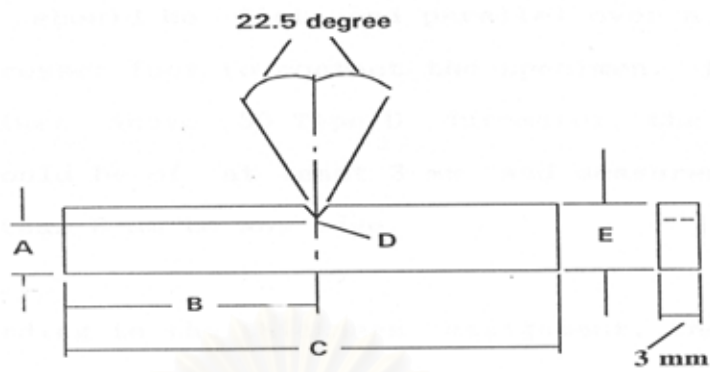
Figure 3.15 A Gotech GP-7045 MD Pendulum impact tester (Izod-type)

The machine parameters and testing conditions of the impact test were listed below:

Temperature:	25°C
Relative humidity:	50%

The specimen shows in Figure 3.16.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



A: 10.16 ± 0.05 mm B: 32.00 max, 31.50 min
 C: 63.50 max, 53.50 min D: 0.25 ± 0.05 mm
 E: 12.70 ± 0.15 mm

Figure 3.16 Schematic of Izod-type test specimen

สถาบันวิทยบริการ
 จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristics of Surface-modified and Unmodified Polypropylene Nonwovens

PP nonwoven was surface-modified using UNU/ICTP plasma focus device as shown in Figure 3.4. Samples of PP nonwoven having dimensions of 13 cm x 9 cm were placed on the cover and the position 1,2,3 respectively in the chamber of UNU/ICTP plasma focus device as shown in Figure 3.5. The plasma focus device was then operated using nitrogen or oxygen gas at a pressure of 1.5 mbar and discharge voltage at 12.5 kV. The number of plasma shots used was at 4 shots which was the suitable condition for surface modification of PP nonwoven at the cover position reported by J. Srisawat [49]. After the process completed, PP nonwoven samples were removed from the chamber and subjected to further characterization.

4.1.1 Morphology

SEM images of unmodified PP nonwoven shown in Figure 4.1a show that PP nonwoven consists of long polypropylene fibers bound together at a position having square shape. Also, these polypropylene fibers have smooth surface. After plasma exposure, SEM images show an increase in the roughness of the fiber surface as shown in Figures 4.1 b-e and Figures 4.2 b-e. It can be seen that oxygen and nitrogen plasmas caused chain scission due to bombardment of high energy reactive plasma species. Furthermore, it was also observed that some parts of filament swelled or melted together due to the heat generated in the device. When considering the effect of the positions placing the samples, it was found that placing the sample at cover position resulted in the highest change in the surface roughness as shown in Figures 4.1 b and 4.2 b. These results are corresponding to the dynamic principle of plasma focus device which is that the focusing phase occurs at the cover position [44].

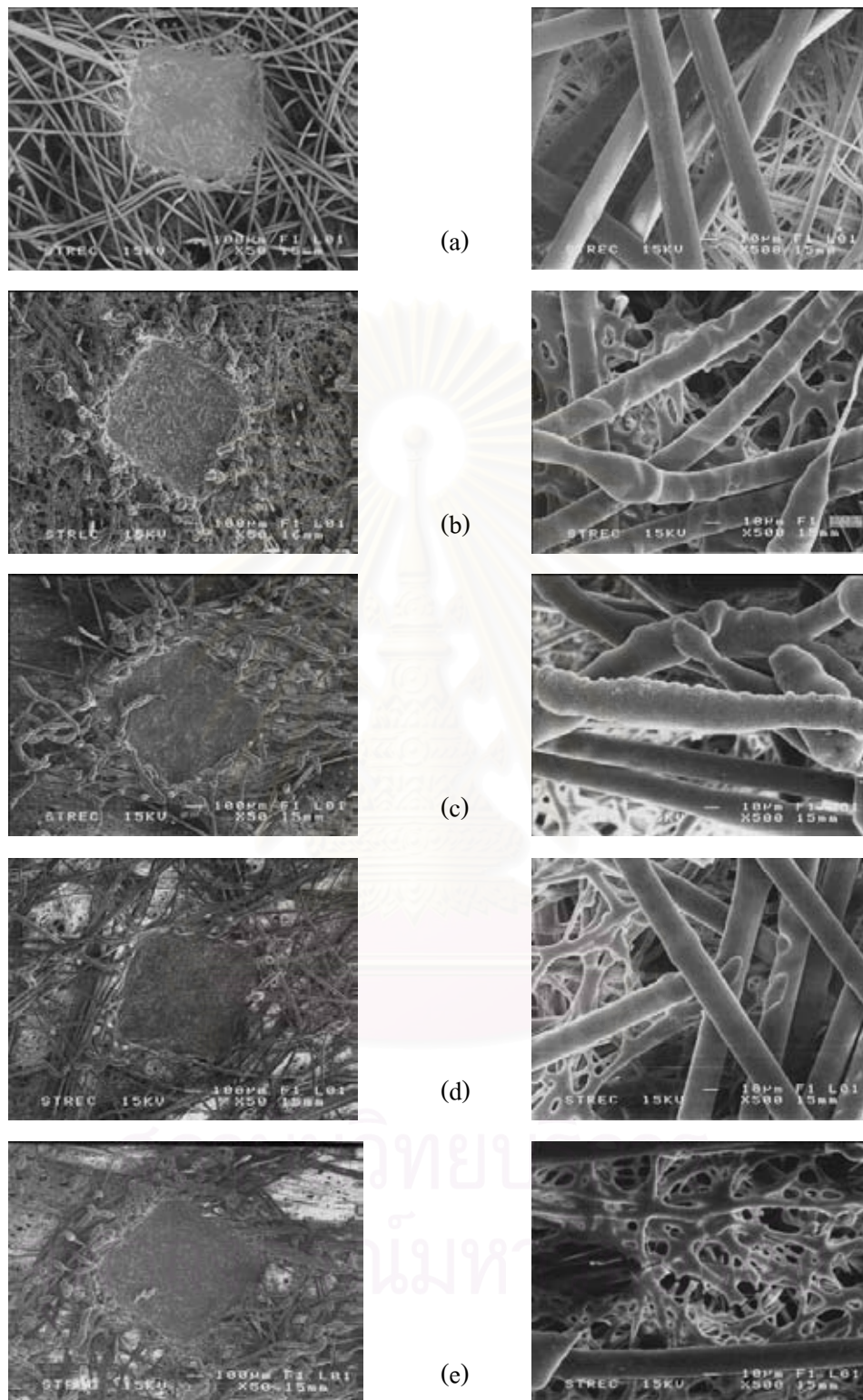


Figure 4.1 SEM images of unmodified PP nonwoven (a), oxygen plasma-modified PP nonwovens: cover position (b), position 1 (c), position 2 (d), and position 3 (e)

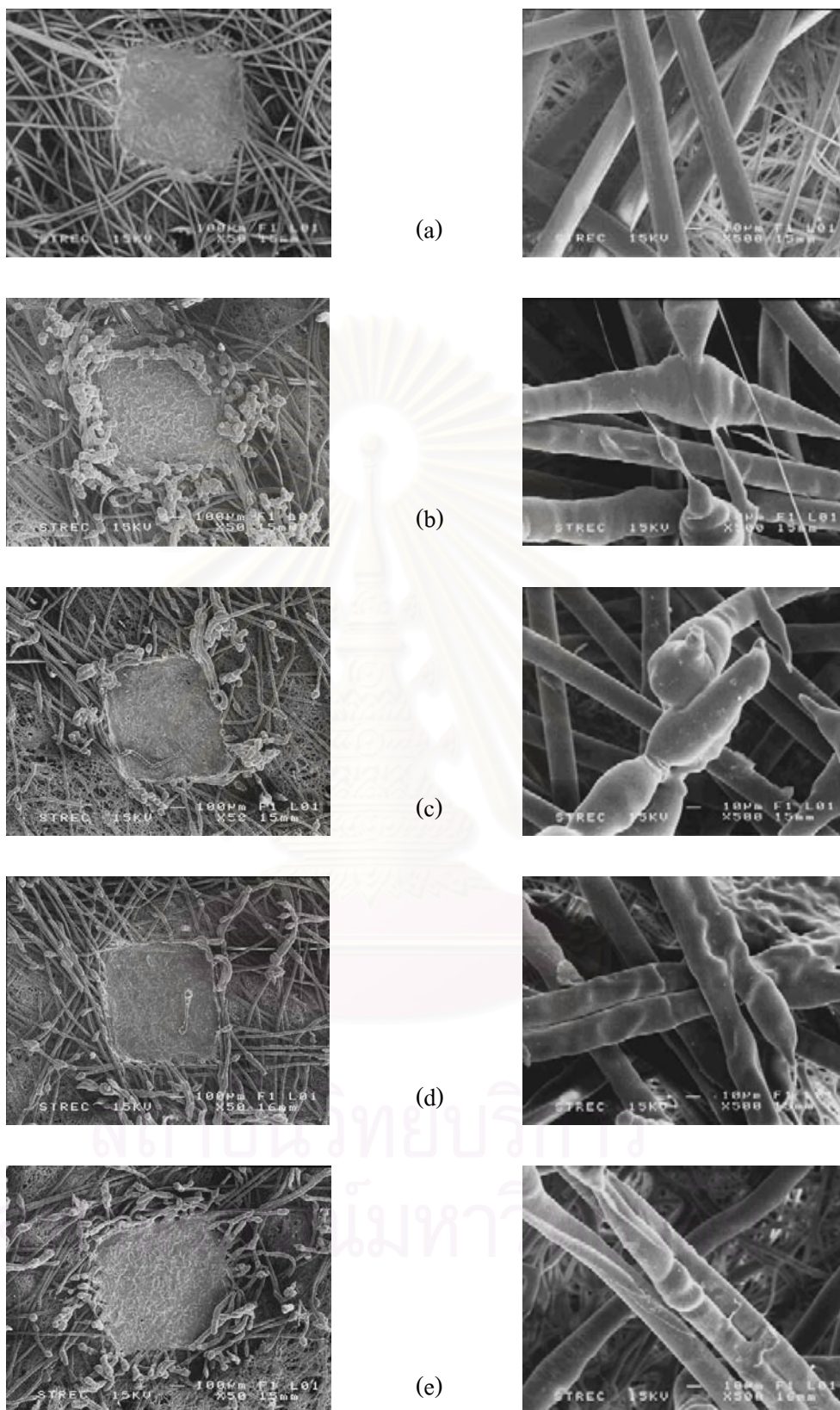


Figure 4.2 SEM images of unmodified PP nonwoven (a), nitrogen plasma-modified PP nonwovens: cover position (b), position 1 (c), position 2 (d), and position 3 (e)

4.1.2 Water Contact Angle

Contact angle measurement is a very useful technique in many fields such as adhesion, surface treatment, and polymer surface modification, to measure the hydrophilicity of solid surface, related to surface energy and surface tension. The contact angle depends on the chemical composition of the surface and on its morphology. If the surfaces show higher hydrophobic properties, the higher water contact angle is presented. On the other hand, the lower contact angles results in hydrophilic properties.

The water contact angles of unmodified, oxygen plasma-modified and nitrogen plasma-modified PP nonwovens are shown in Table 4.1

Table 4.1 Water contact angles of unmodified, oxygen plasma-modified and nitrogen plasma-modified PP nonwovens

Type of PP nonwoven	Water contact angle (degree)	
	nitrogen	oxygen
unmodified	111 ± 3	111 ± 3
position 1	108 ± 3	101 ± 3
position 2	102 ± 1	100 ± 2
position 3	105 ± 4	102 ± 4
cover position	98 ± 2	97 ± 1

As shown in the above table, all plasma-modified PP nonwovens at every position exhibit lower water contact angles than unmodified PP nonwoven. From these results, it can be assumed that plasma treatment leads to the formation of hydrophilic groups on the surface of PP nonwoven.

However, PP nonwovens both treated with nitrogen and oxygen plasmas placed on the cover position exhibited lowest water contact angles when compared to those placed at other positions. Since in plasma focus device, the focusing phase mainly occurred at this position, therefore, it can be expected that the amounts of functional groups formed at this position may be higher than at other positions.

Furthermore, it can be seen from this table that nitrogen plasma-modified PP nonwovens have higher water contact angles than oxygen plasma-modified PP nonwovens. This suggests that the type of functional groups incorporated onto the surface depend upon the type of gases used for modification. It also indicates that the functional groups formed on the latter are more hydrophilic than those formed on the former.

4.1.3 Chemical Structure

Figure 4.3 shows ATR-FTIR spectra of unmodified and oxygen plasma-modified PP nonwovens placed at different positions in the chamber. After treating with oxygen plasma, it can be observed that the intensities of the peak corresponding to O-H stretching of hydroxyl group (OH) at wavenumber of $3400\text{-}3500\text{ cm}^{-1}$ relatively increase and the intensity of the peak attributed to C-H stretching of CH_2 group at wavenumber of 2837 cm^{-1} relatively decrease. However, the observation is not clearly seen due to low amount of OH groups was formed.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

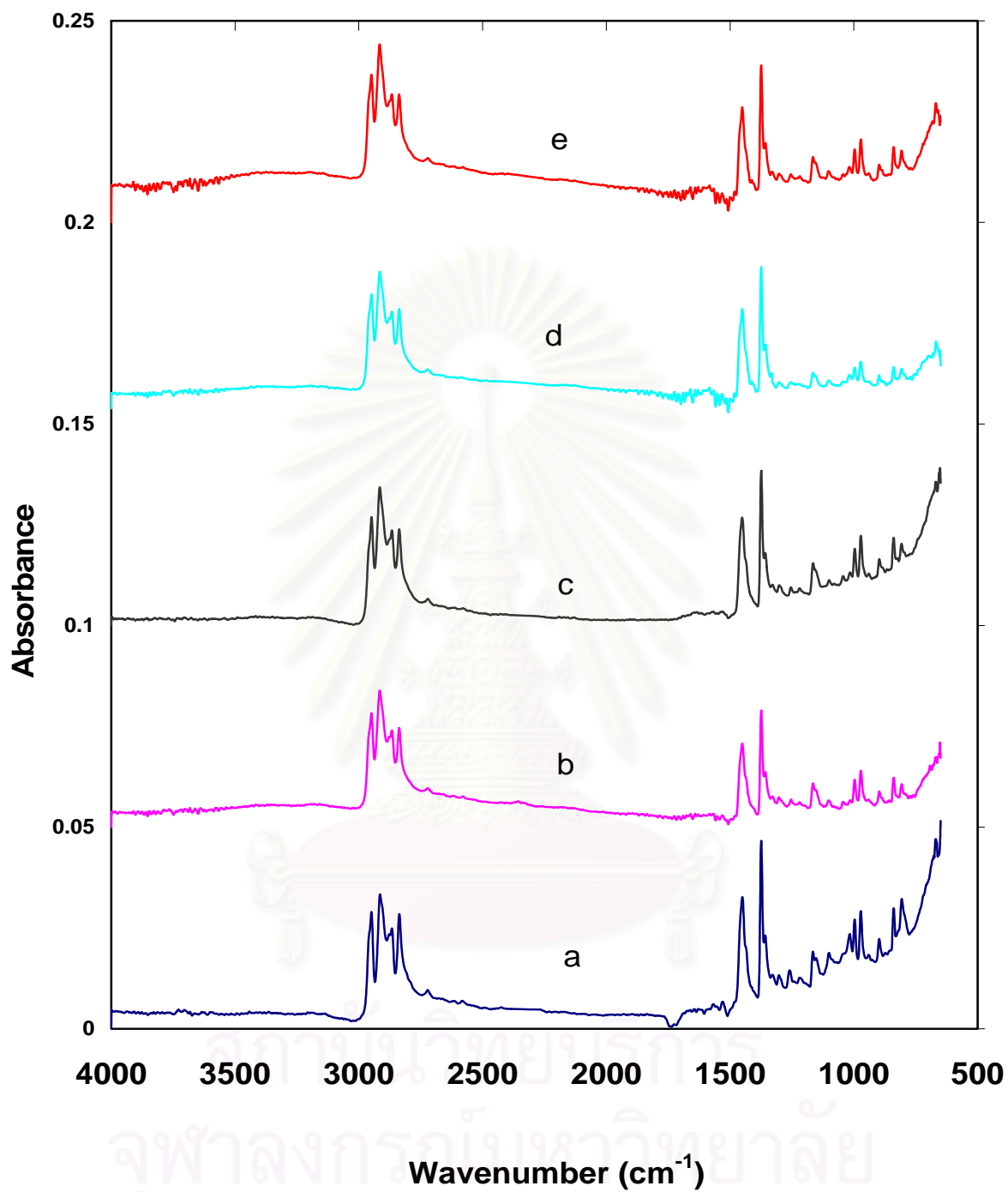


Figure 4.3 ATR-FTIR spectra of unmodified PP nonwoven (a) and oxygen plasma-modified PP nonwovens: cover position (b), position 1 (c), position 2 (d) and position 3 (e)

As was reported by Inagaki [31], oxygen plasma-modified can cause the formation of many functional groups such as carboxylic, aldehyde, ketone, etc. As for this research, the following mechanism in Figure 4.4 was proposed for oxygen plasma treatment on PP nonwoven.

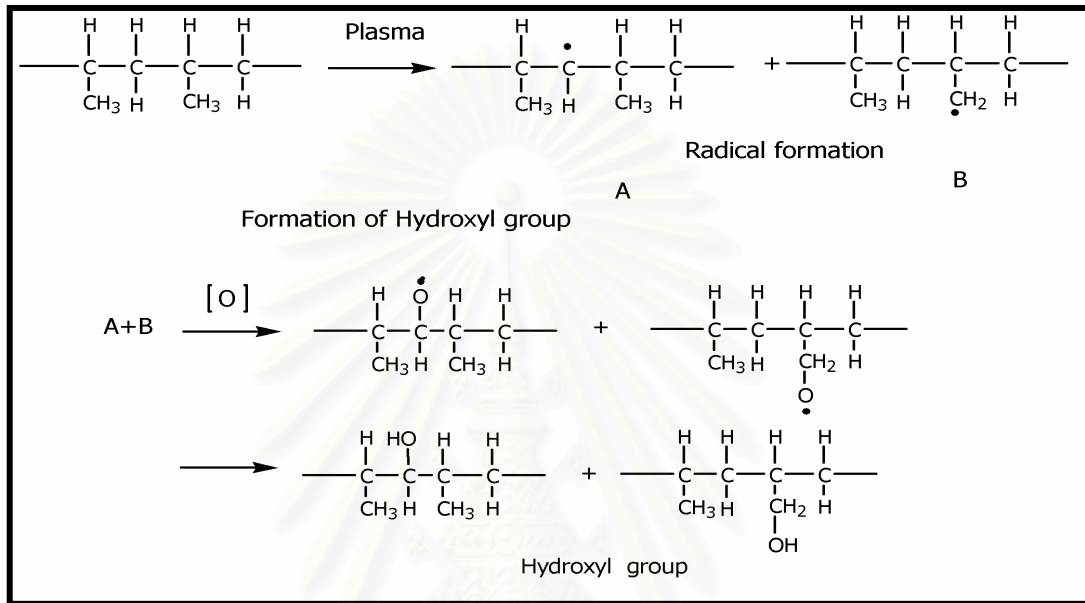


Figure 4.4 Proposed mechanism of oxygen plasma treatment on PP nonwoven

Consideration the surface of PP nonwoven after exposed to nitrogen plasma. It was reported by Inagaki et al [31] that such functional groups can be nitrogen-containing groups. The possible mechanism for the formation of nitrogen-containing groups such as amino (NH_2) and azo (-N=N-H) groups can be proposed as follows:

จุฬาลงกรณ์มหาวิทยาลัย

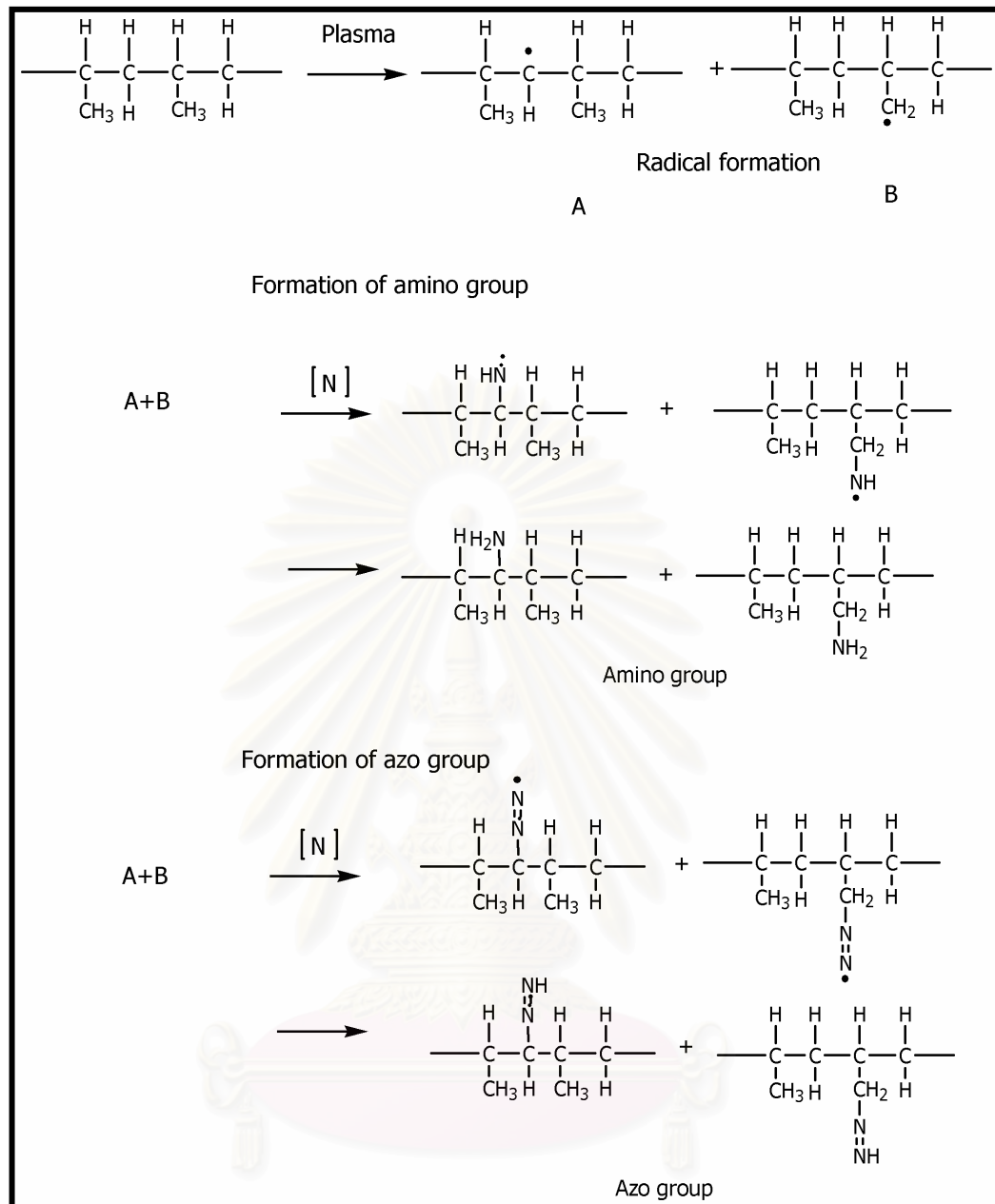


Figure 4.5 Proposed mechanism of nitrogen plasma treatment on PP nonwoven

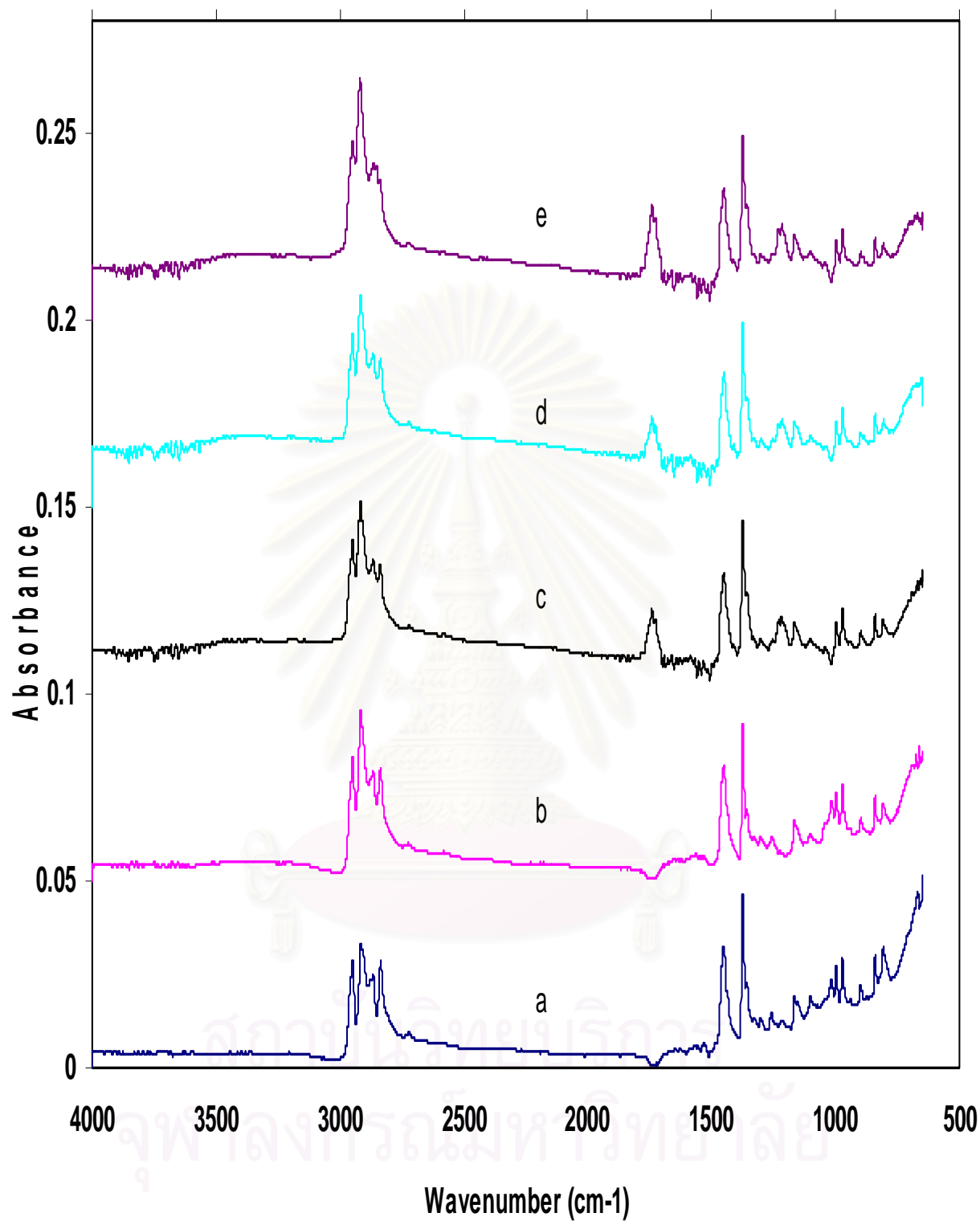


Figure 4.6 ATR-FTIR spectra of unmodified PP nonwoven (a) and nitrogen plasma-modified PP nonwovens: cover position (b), position 1 (c), position 2 (d) and position 3 (e)

From the proposed mechanism in Figure 4.5, it is clearly seen from Figure 4.6 that nitrogen plasma-modified PP nonwovens placed at positions 1, 2 and 3 exhibit the peak corresponding to N=N stretching at wavenumber of 1740 cm^{-1} . These results suggest the formation of azo groups (-N=N-H) on PP surface. On the other hand, PP nonwoven placed at cover position does not show this peak, this suggests a possibility that at this position, other type of functional group is formed. When compared to FT-IR spectrum of unmodified PP nonwoven as shown in Figure 4.6, a relative increase in the intensity of the peak corresponding to N-H stretching of amine group (NH_2) at wavenumber of $3400\text{-}3500\text{ cm}^{-1}$ and a relatively decrease the intensity of the peak attributed to C-H stretching of CH_2 group at wavenumber of 2837 cm^{-1} , respectively are observed in FT-IR spectra of surface-modified PP nonwovens. However, the observation is not clearly seen due to low amount of OH groups was formed.

4.2 Mechanical Properties of Polypropylene-Polyester/Cotton Composites

Polypropylene-Polyester/Cotton (PP-PET/C) composites were prepared by compression molding. Both unmodified and modified PP nonwovens were compressed with PET/C nonwoven at 190°C for 12 minutes. Comparison of the mechanical properties of PP-PET/C composites with those of pure polypropylene is presented in this section. This section will focus on the effects of the treatment position of PP nonwoven in the chamber and the type of gas on impact, tensile and flexural properties of PP-PET/C composites.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

4.2.1 Impact Strength

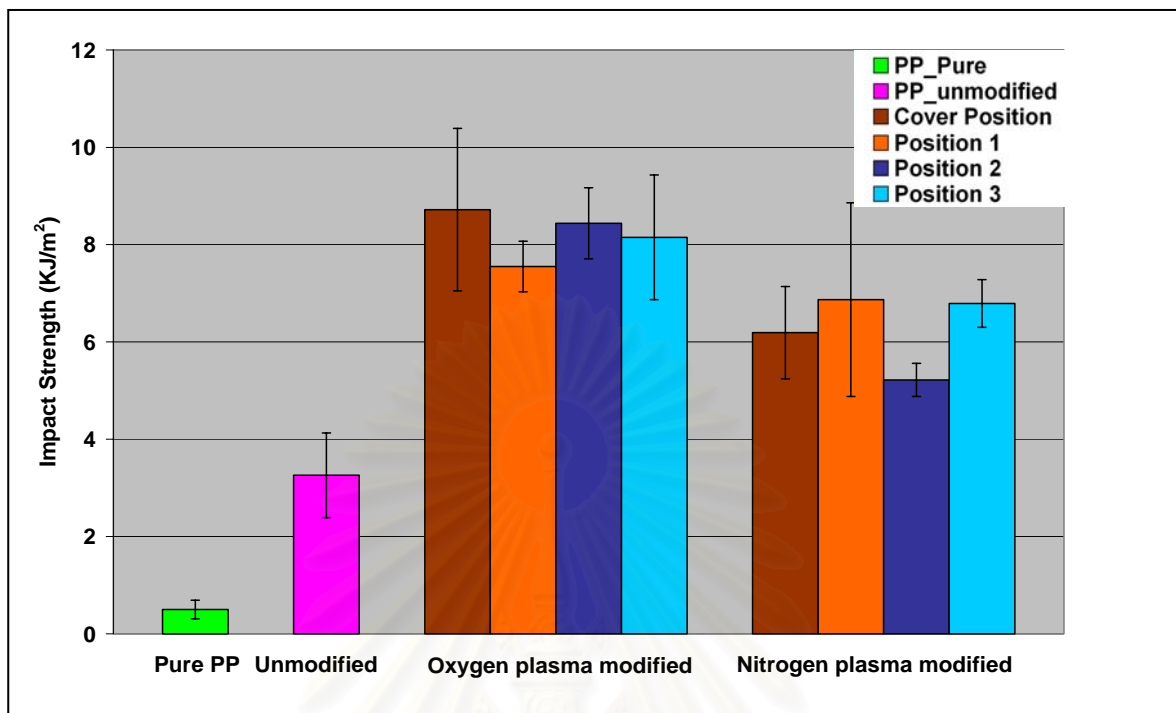


Figure 4.7 Impact strength of polypropylene and polypropylene-polyester/cotton composites

It is clearly seen from Figure 4.7 that surface modification of PP nonwoven by plasma treatment directly affects the impact strength of the composites. Unmodified PP-PET/C composite presents an increase in impact strength compared to pure PP. This is due to the introduction of more flexible PET/C molecules in PP matrix leading to an improvement in impact strength.

Figure 4.7 indicates great improvement of impact strength of the composites by plasma modification. Both oxygen and nitrogen plasma-modified PP-PET/C composites exhibit much higher impact strength than unmodified PP-PET/C composites and PP. This is a result of an enhancement of surface adhesion between plasma-modified PP matrix and PET/C filler caused by hydrogen bonding between hydrophilic functional groups on PP and PET/C molecules as confirmed by ATR-FTIR spectra. In addition, this enhancement is also caused by an increase in adhered area between these two components resulting from

increasing roughness after plasma exposure as confirmed by SEM photographs. Therefore, energy transfer after the samples subjected to impact load was better.

In addition, when determining the effect of the gas type, it is clearly seen that impact strength of oxygen plasma-modified PP-PET/C composites is higher than nitrogen plasma-modified PP-PET/C composites since in oxygen plasma treatment more hydrophilic functional groups were formed as confirmed by water contact angle measurement. Consequently, for oxygen plasma-modified PP-PET/C composites, higher interaction between PP matrix and PET/C filler occurred.

Furthermore, when the same gas was used, it was found that the impact strength of plasma-modified composites prepared from PP nonwovens placed at different positions in the chamber were different. This may be due to the difference in the amount and/or the type of hydrophilic functional groups formed on PP molecules and also the difference in adhered areas as previously explained.

4.2.2 Tensile Properties

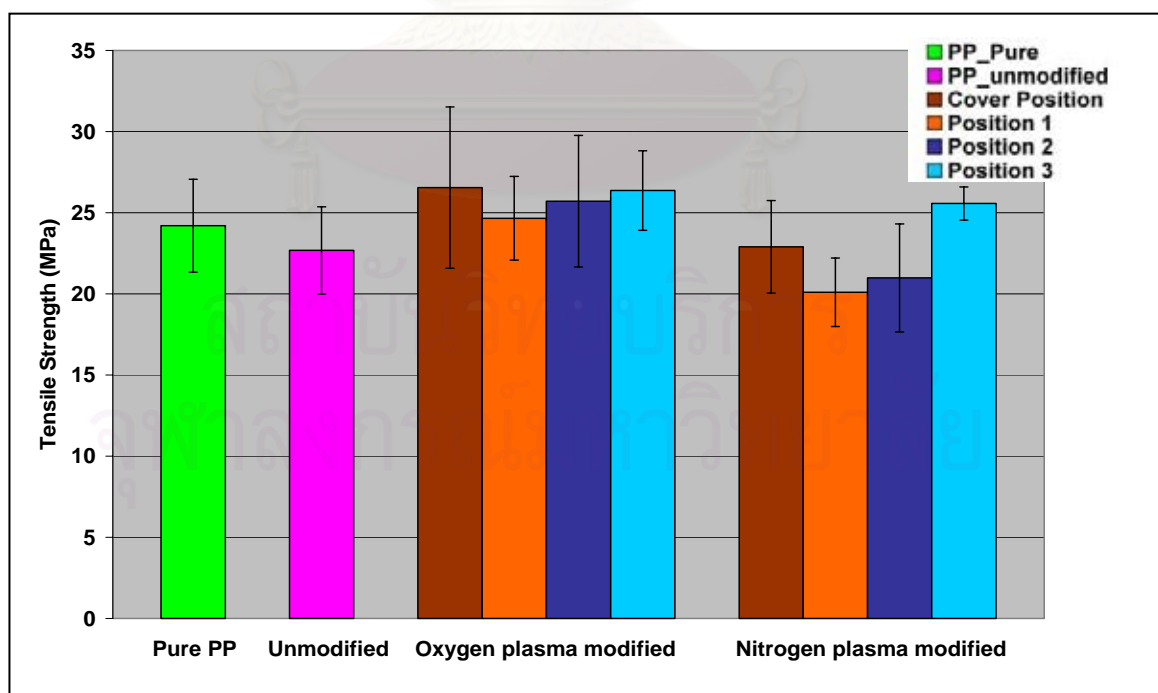


Figure 4.8 Tensile strength of polypropylene and polypropylene-polyester/cotton composites

It is clearly seen from Figure 4.8 that surface modification of PP nonwoven by plasma treatment significantly affects the tensile strength of PP-PET/C composites. Unmodified PP-PET/C shows lower tensile strength than pure PP. This is due to the difference in hydrophilic characteristic between these two components of the composites. Adding hydrophilic PET/C filler into hydrophobic PP matrix would result in low surface adhesion between these two components causing the defects in the samples. As a result, lower tensile strength was observed.

The effects of plasma treatment on tensile strength can be divided into 2 effects: positive and negative effects. The positive effect is attributed to the formation of hydrophilic functional groups on PP surface resulting in higher interaction between PP matrix and PET/C filler and an increase in adhered area on PP surface after plasma exposure. This can increase the tensile strength of the composites. On the other hand, the negative effect is a result of the chain rupture of PP molecules reducing PP molecular weight and lowering the tensile strength. Therefore, the tensile strength of plasma-modified PP-PET/C composites will depend on these two effects. In the case of oxygen plasma-modified PP-PET/C composites, the results shown in Figure 4.8 suggest that the positive effect dominates since all samples exhibit higher tensile strength than unmodified PP-PET/C composite and pure PP. In contrast to the former, the negative effect plays an important role in affecting the tensile strength of nitrogen plasma-modified PP-PET/C composites. Consequently, most of these composites have comparable or lower tensile strength than unmodified PP-PET/C composite and pure PP.

When the same gas was used, it was found that due to different adhered areas and types and/or amounts of hydrophilic functional groups formed on the surface of PP nonwovens placed at different positions in the chamber as previously described, the tensile strength of plasma-modified PP-PET/C composites prepared from PP nonwovens placed at different positions in the chamber are different as shown in Figure 4.8.

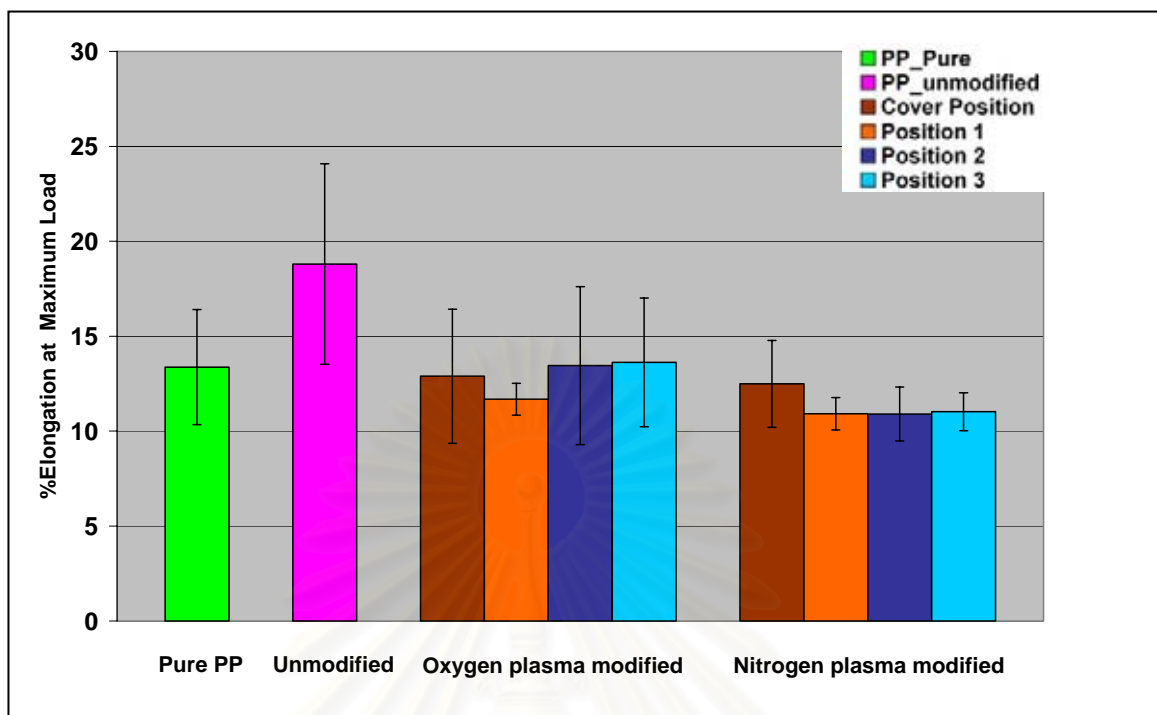


Figure 4.9 %Elongation at maximum load of polypropylene and polypropylene-polyester/cotton composites

It can be seen from Figure 4.9 that unmodified PP-PET/C composite has higher %elongation than pure PP due to the presence of PET/C filler. Adding PET/C filler to PP matrix disturbs the orientation of PP molecules; hence, less crystalline regions are formed when compared to pure PP. Therefore, it is easier for all polymer molecules present in the composite to slide by each other when compared to those present in pure PP.

However, after plasma treatment, all plasma-modified PP-PET/C composites exhibit lower %elongation than the unmodified one. This may be attributed to higher interaction between PET/C filler and plasma-modified PP matrix. This prevents the polymer molecules to move apart from each other after subjecting to tensile load.

From Figure 4.9, it can be assumed that the treatment position does not significantly affect %elongation of plasma-modified composites since their %elongation are comparable. On the other hand, the type of gas shows slightly effect on this property of plasma-modified

composites. Since oxygen plasma treatment results in the formation of more hydrophilic functional groups than nitrogen plasma treatment, the interaction between all polymer molecules in the former system should be higher and it can be expected that %elongation of the former system should be lower than that of the latter system. However, from Figure 4.9, it can be seen that oxygen plasma-modified PP-PET/C composites have slightly higher %elongation than nitrogen plasma-modified PP-PET/C composites. This may possibly be because those more hydrophilic groups of oxygen plasma-modified composites can attract and absorb more moisture. Jetsadang [49] The moisture molecules can facilitate the movement of polymer molecules. Therefore, the above results were observed.

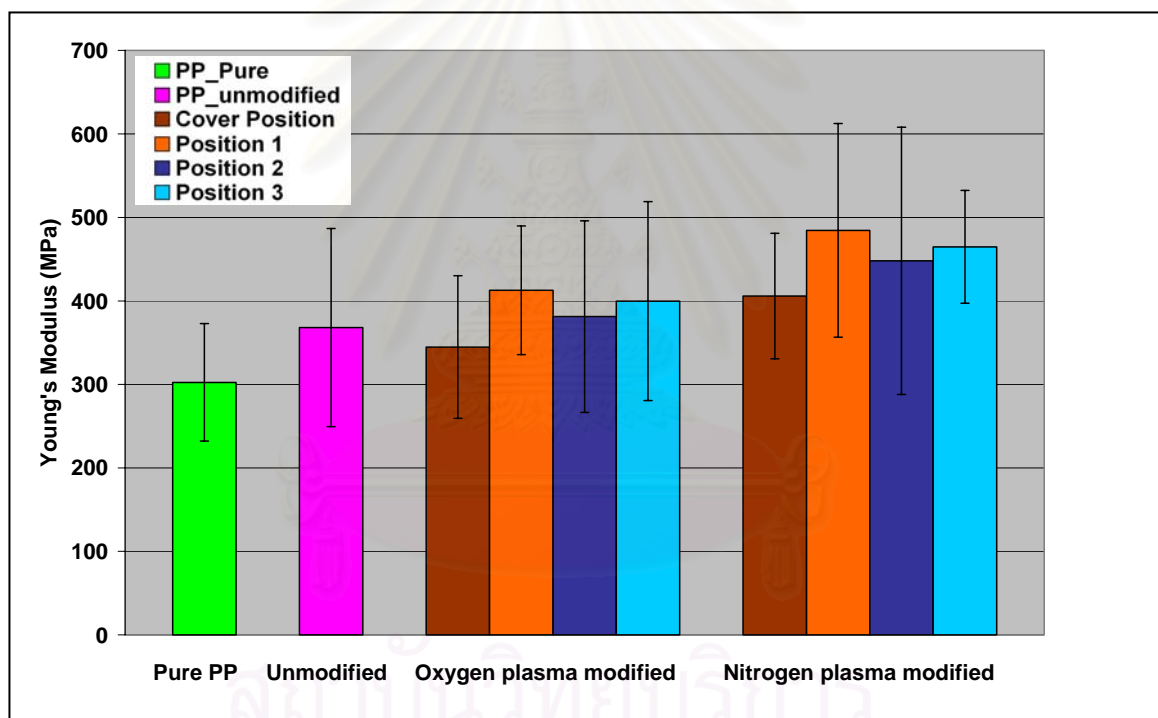


Figure 4.10 Young's modulus of polypropylene and polypropylene-polyester/cotton composites

When considering the effect of surface modification by plasma treatment on Young's modulus, it is clearly seen that an increase in surface adhesion between PET/C filler and PP matrix results in an increase in Young's modulus of the composites. However, since the movement of polymer molecules in oxygen plasma-modified composites is easier than that

of those in nitrogen plasma-modified composites as previously discussed; consequently, Young's modulus of the former is lower than that of the latter.

When the same gas was used, it was found that due to different adhered areas and types and/or amounts of hydrophilic functional groups formed on the surface of PP nonwovens placed at different positions in the chamber as previously described, Young's modulus of plasma-modified PP-PET/C composites prepared from PP nonwovens placed at different positions in the chamber are different as shown in Figure 4.10.

4.2.3 Flexural Properties

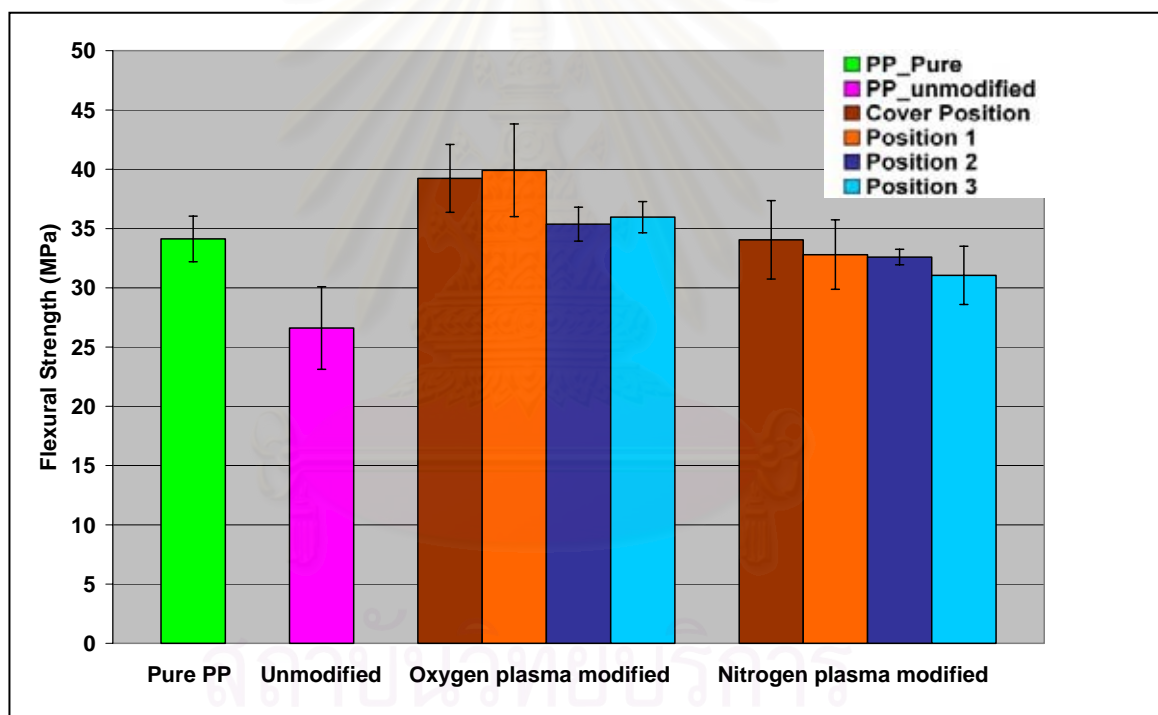


Figure 4.11 Flexural strength of polypropylene and polypropylene-polyester/cotton composites

Figure 4.11 shows that the effect of surface modification by plasma treatment on flexural strength of PP-PET/C composites is quite similar to that of tensile strength. Flexural strength also increases with increasing surface adhesion between PP and PET/C molecules

which is caused by a presence of hydrophilic groups and an increase in adhered area on PP surface after plasma exposure.

Figure 4.11 also shows that flexural strength of oxygen plasma-modified PP-PET/C composites is higher than that of nitrogen plasma-modified PP-PET/C composites due to the formation of more hydrophilic functional groups as previously discussed. However, the effect of the positions placing the samples can not be obviously seen here.

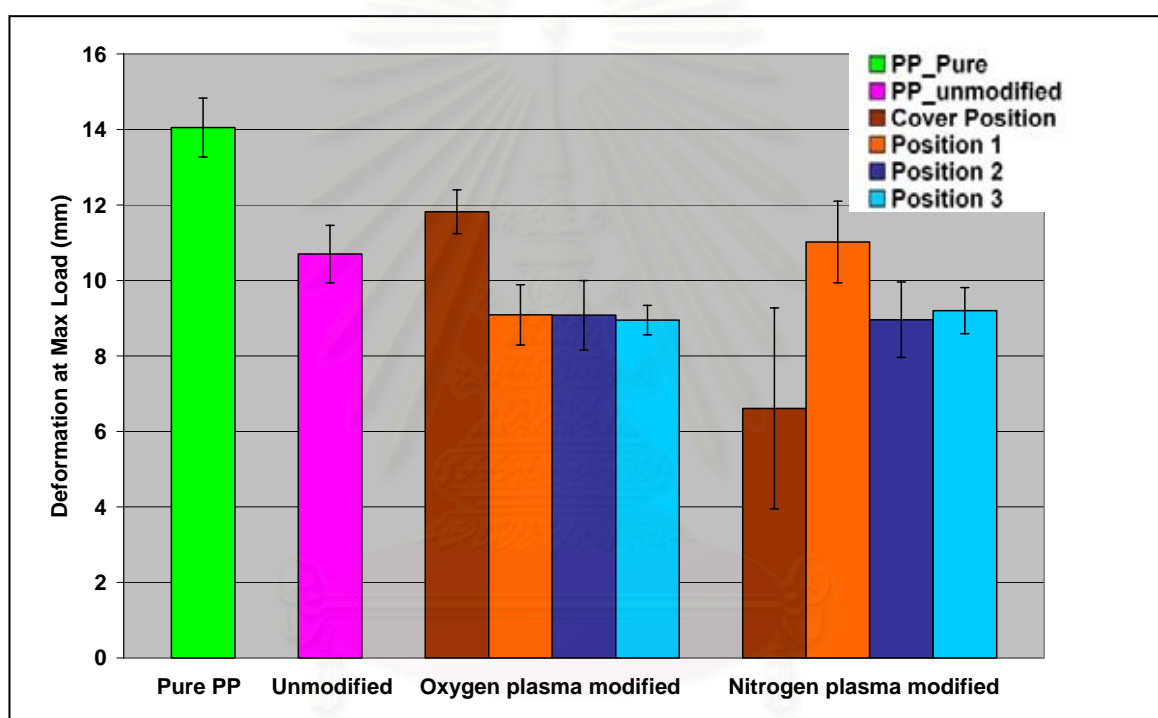


Figure 4.12 Deformation at maximum load of polypropylene and polypropylene-polyester/cotton composites

Figure 4.12 shows the effect of plasma treatment on the deformation of PP-PET/C composites. As surface adhesion between the two components increases, it is more difficult for polymer molecules to move apart from each other. Therefore, deformation of plasma-modified composites tends to decrease when compared to that of the unmodified composite.

Furthermore, it is clearly seen from this figure that the positions placing the samples significantly affect this property. In the case of oxygen plasma treatment, the composite prepared from PP nonwoven placed at cover position exhibited higher deformation than those prepared from PP nonwovens placed at other positions. This suggests that at this position where higher amount of hydroxyl groups are formed, the plasticization effect of moisture molecules absorbed by these hydroxyl groups overshadows the formation of hydrogen bonding between these functional groups with hydrophilic functional groups on PET/C filler.

In the case of nitrogen plasma treatment, the composite prepared from PP nonwoven placed at cover position exhibited lower deformation than those prepared from PP nonwovens placed at other positions. This is because, at this position, amine group which is more hydrophilic than azo group is formed as previously mentioned; therefore, higher adhesion can occur and it is more difficult for polymer molecules to move apart from each other.

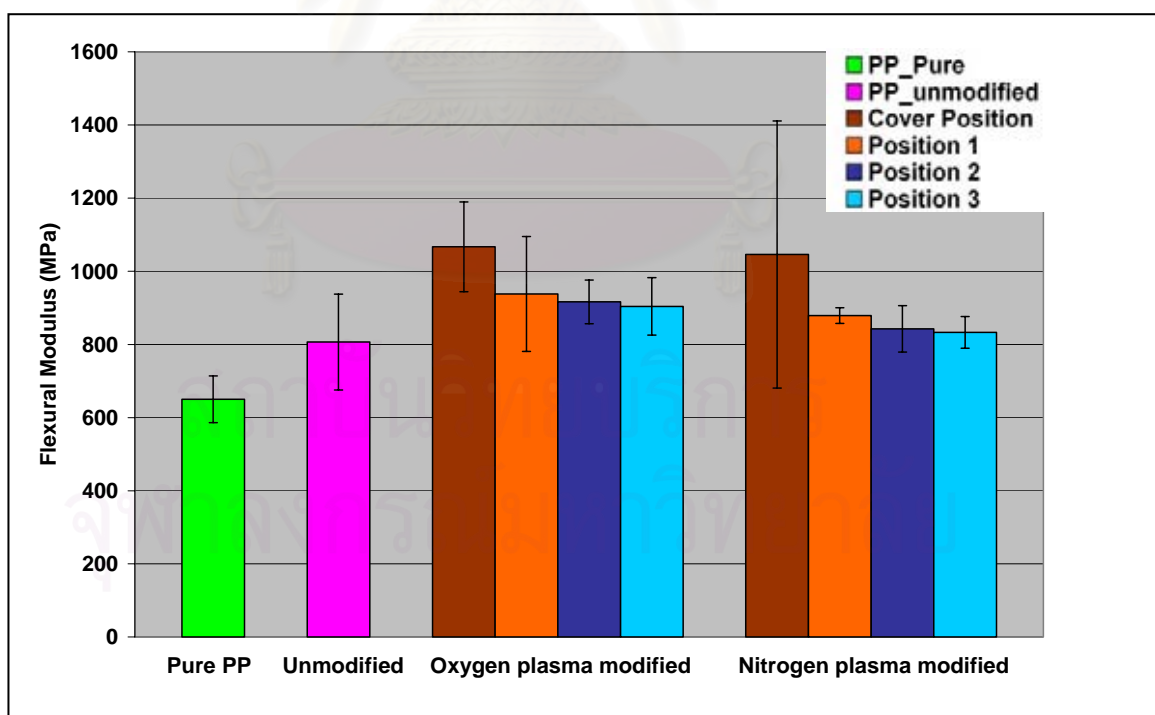


Figure 4.13 Flexural modulus of polypropylene and polypropylene-polyester/cotton composites

Figure 4.13 shows that the effect of surface modification by plasma treatment on flexural modulus of PP-PET/C composites is quite similar to that of Young's modulus. It is clearly seen that an increase in surface adhesion between PET/C filler and PP matrix results in an increase in flexural modulus of the composites. The effect of the gas type on this property is not clearly observed whereas the position in the chamber significantly affects this property. When the same gas was used, it was found that due to increasing adhered area and higher amount of hydrophilic functional groups formed on the surface of PP nonwovens placed at cover position as previously described, flexural modulus of plasma-modified PP-PET/C composites prepared from PP nonwovens placed at this position is higher than those of the composites prepared from PP nonwovens placed at other positions.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this research, surface modification of PP nonwoven by high temperature pulsed-plasma generated from UNU/ICTP Plasma Focus device prior to preparation of PP-PET/C composites was studied. The effects of the gas type and the treatment position of PP nonwoven in the chamber on mechanical properties of the obtained composites were also investigated. The results can be concluded as follows:

1. All plasma-modified PP nonwovens exhibited surface roughness resulted from chain rupture and swelling of the fibers as revealed in SEM photographs.

2. From FT-IR spectroscopic analysis and water contact angle measurement, it was found that hydrophilicity of plasma-modified PP nonwovens was higher than that of the unmodified one. The type and amount of hydrophilic functional groups formed on PP surface depended on the gas type and the treatment position.

3. All plasma-modified PP-PET/C composites exhibited superior impact strength when compared to PP plastic and the unmodified composite as a result of an enhancement of surface adhesion between PP matrix and PET/C filler. Due to more hydrophilic functional groups formed in oxygen plasma treatment, oxygen plasma-modified composites had higher impact strength than those modified with nitrogen plasma. However, the treatment position did not significantly affect this property.

4. All plasma-modified composites exhibited lower %elongation at maximum load and higher Young's modulus than PP plastic and unmodified composite. However, due to the differences in type and amount of hydrophilic functional groups formed, surface roughness and chain rupture on PP surface, oxygen plasma-modified composites exhibited

higher tensile strength while nitrogen plasma-modified composites showed lower tensile strength than PP plastic and the unmodified composite.

5. All plasma-modified composites had higher flexural strength and flexural modulus but lower deformation at maximum load than unmodified composite. Both the gas type and the position the samples were placed in the chamber were the main factor affecting the deformation at maximum load. The results showed that placing PP nonwovens at the cover position yielded the composites having highest deformation in oxygen plasma treatment but resulted in the composites having lowest deformation in nitrogen plasma treatment.

The above results suggested that using oxygen plasma treatment resulted in the composites having better mechanical properties than using nitrogen plasma treatment. Furthermore, it can be concluded that in oxygen plasma treatment, placing PP nonwoven directly on top of the focusing position (cover position) yielded the composites having better mechanical properties than at the sides of the chamber. On the other hand, in nitrogen plasma treatment, placing PP nonwoven at the sides of the chamber would result in the composites having better mechanical properties. Overall results indicated that the composite prepared from PP nonwoven surface-modified by oxygen plasma and placed directly on top of the focusing position had the best mechanical properties.

5.2 Recommendations

1. In order to determine exact reaction mechanisms between nitrogen and oxygen plasmas and PP molecules, further studies using more sophisticated techniques such as x-ray photoelectron spectroscopy should be employed.

2. Since the number of plasma shots used in this research was based on the suitable condition for surface modification of PP nonwoven at cover position reported by J. Srisawat [49], it is interested to change the number of plasma shots in order to find the suitable condition for surface modification of PP nonwoven at the sides of the chamber.

3. The effects of other types of gases, charging voltage and pressure on the characteristics of PP nonwoven and the mechanical properties of obtained composites should be studied.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

REFERENCES

1. Gibson, R.F. Principles of Composite Material Mechanics. New York : Mc Graw-Hill, 1994.
2. www.science.org.au/nova/059/059key.htm. (accessed on 13/12/2005).
3. Schwartz, M.M. Composite Materials. U.S.A : PTR Prentice Hall, 1996 : 9.
4. Richardson, T. Composites: A Design Guide. New York : Industrial Press Inc., 1987.
5. Gachter, R., Muller, H. Plastics Additives Handbook. New York : Houser Pulishers, 1987.
6. Brydson, J.A. Plastic Materials. London : Mansell, 1982 : 225-227.
7. Odian, G. Principle of Polymerization. 3rd ed. New York : John Wiley & Son, 1990 : 657.
8. Wypych, G. Handbook of Fillers. 2nd ed. Canada : Chem Tec Publishing, 2000 : 890.
9. Demianiw, D.G. Olefin Polymer (polypropylene). Encyclopedia of Chemical Technology. 16 (1981) : 454.
10. Xanthos, M. Functional Fillers for Plastics. Geramany : Wiley-VCH, 2005.
11. Skatz, H., Milewski, J.V. Handbook of Fillers and Reinforcements for Plastics. New York : Van Nostrand Reinhold, 1978.
12. Colling, D.A., Vasilos, T. Industrial Materials. Vol.2. New Jersey : Prentice-Hall, 1995.
13. Jone, R.F. Guide to Short Fiber Reinforced Plastics. Munich : Hanser Publishers, 1998.
14. Schwartz, M.M. Composite Materials : Properties, Nondestructive Testing and Repair. Vol.1. New Jersey : Prentice Hall PTR, 1997.
15. Feldmand, D., Barbalate, A. Synthetic Polymer Technology, Properties, Application. London : Chapman&Hall, 1996 : 177-182.
16. Karmaka, S.R. Chemical Technology in the Pre-Treatment Processes of Textile. New York : Elsevier, 1999.
17. Colling, D.A and Vasilos, T. Industrial Materials. Vol.2. New Jersey : Prentice-Hall, 1995.

18. Agarwal, B.D., Brout, L.J. Analysis and Performance of Fiber Composite.
U.S.A. : John Wiley & Sons, 1980 : 3.
19. <http://info.lu.farmingdale.edu/depts/met/met205/composites.html>. (accessed on 14/12/2005).
20. http://www.mdi.espci.fr/~chateau/COURS/Composites/Applet_comp/transfert/transfert_en/index_en.html. (accessed on 14/12/2005)
21. <http://www.mse.cornell.edu/courses/engri111/fiber.htm>.(accessed on 14/12/2005)
22. Shibata, S., Cao, Y., Fukumoto, I. Lightweight laminate composites made from kenaf and polypropylene fibres. Polymer Testing 25 (2006) : 142–148.
23. Bullions, T.A., Hoffman, D., Gillespie, R.A., Brien, J.P.O., Loos, A.C. Contributions of feather fibers and various cellulose fibers to the mechanical properties of polypropylene matrix composites. Composites Science and Technology 66 (2006) : 102–114.
24. Arib, R.M.N., Sapuan, S.M., Ahmad, M.M.H.M., Paridah, M.T., Zaman, K.H.M.D. Mechanical properties of pineapple leaf fiber reinforced polypropylene composites. Journal of Materials & Design 27 (2006) :391-396.
25. <http://www.wipo.int/ipdl/IPDLCIMAGES/view/pct/getbykey5?KEY=98/06551.980723>. (accessed on 15/03/2006).
26. Karger-Kocsis, J. Polypropylene: Composites. Vol.3. London : Chapman & Hall, 1995.
27. [http://taylorandfrancis.metapress.com/\(tazwrf45c30fcl4541igmk55\)/app/home/contribution.asp?referrer=parent&backto=issue,9,9;journal,34,37;linkingpublicationresults,1:104793,1](http://taylorandfrancis.metapress.com/(tazwrf45c30fcl4541igmk55)/app/home/contribution.asp?referrer=parent&backto=issue,9,9;journal,34,37;linkingpublicationresults,1:104793,1). (accessed on 15/03/2006).
28. Felix, J.M., Gatenholm, P. The nature of adhesion in composites of modified cellulose fibers and polypropylene. Journal of Applied Polymer Science 42 (1991) : 609-620.
29. Arbelaiz, A., Fernandez, B., Cantero, G., Llano-Ponte, R., Valea, A., Mondragon, I. Mechanical properties of flax fibre/polypropylene composites. Influence of fibre/matrix modification and glass fibre hybridization. Journal of Composites 36 (2005) : 1637-1644.

30. Doan, T. T.L., Gao, S.L., Mader, E. Jute/polypropylene composites I. Effect of matrix modification. Composites Science and Technology (2005) : in press.
31. Inagaki, N. Hydrophilic Surface (Plasma Treatment and Plasma Polymerization) Surfaces, 3115-3123. : CRC Press, 1996.
32. Huang, F., Wei, Q., Wang, X., Xu, W. Dynamic contact angles and morphology of PP fibers treated with plasma. Polymer Testing 25 (2006) : 22-27.
33. Hwang, Y., J. Characterization of atmospheric pressure plasma interaction with textile/polymer substrate. Doctor of Philosophy, Faculty of Fiber and Polymer Science, North Carolina State University. (2003).
34. http://www.astp.com/PDFs/PS_Cleaning_&_Adhesion.pdf. (accessed on 14/12/2005).
35. Inagaki, N., Tasaka, S., Narushima, K., Teranishi, K. Surface Modification of Poly (tetrafluoroethylene) with Pulsed Hydrogen Plasma. Journal of Applied Polymer Science 83 (2002) : 340-348.
36. Garbassi, F., Morra, M., Occhiello, E. Polymer Surfaces from Physics to Technology New York : John Wiley & Son, 1994.
37. http://www.marchplasma.com/Pdf/ChipScale1_02_Plasma_Tech%20Forum.Pdf. (accessed on 14/12/2005).
38. Chen, J. Free Radicals of Fibers Treated with Low Temperature Plasma. Journal of Applied Polymer Science 42 (1991) : 2035-2037.
39. Paster, M.C., Kiekens, P. Surface Characteristics of Fibers and Textile. New York : Dekker, 2001.
40. Carrino, L., Moroni, Gand., Polini, W. Cold plasma treatment of polypropylene surface: a study on wettability and adhesion. Journal of Materials Processing Technology 121 (2002) : 373-382.
41. Stepniewski, W. MHD numerical modeling of the plasma focuses phenomena. Vacuum 76 (2004) : 51-55.

42. Bhuyan, H., Mohanty, S.R., Neog, N.K., Bujarbarua, S., Rout, R.K. Magnetic probe Measurements of current sheet dynamics in a coaxial plasma accelerator. Measurement Science and Technology 14 (2003) : 1769-1776.
43. Wong, C.S., Choi, P., Leong, W.S., Singh, J. Generation of high energy ion beams form a plasma focus modified for low pressure operation. The Japan Society of Applied Physics 41 (2002) : 3943-3946.
44. Ngamrunroj, D. Plasma focus modification for material surface treatment. Master's Thesis, Department of Physical Science, Faculty of Science, Chulalongkorn University, 2002.
45. Caiazzo, F., Canonico, P., Nigro, R., Tagliaferri, V. Electrode discharge for plasma surface treatment of polymeric materials. Materials Processing Technology 58 (1996) : 96-99.
46. Rahel, J., Simor, M., Cernak, M., Stefecka, M., Imahori, Y., Kando, M. Hydrophilization of polypropylene nonwoven fabric using surface barrier discharge. Surface and Coatings Technology 169-170 (2003) : 604-608.
47. Wei, Q.F. Studied surface characterization of plasma-treated polypropylene fibers. Materials Characterization 52 (2004) :231-235.
48. Lai, J., Sunderland, B., Xue, J., Yan, S., Zhao, W., Folkard, M., Michael, B.D., Wang, Y. Study on hydrophilicity of polymer surfaces improved by plasma treatment. Applied Surface Science 252 (2006) : 3375–3379.
49. Srisawat, J. Surface modification of polypropylene nonwoven using a plasma focus device for lamination with polyester and cotton nonwoven. Master's Thesis, Department of Materials Science, Faculty of Science, Chulalongkorn University, 2004.



APPENDICES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX A

Experimental Data



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX A

Water Contact Angle of Polypropylene Nonwoven

Table A 1 Experimental data of water contact angle of polypropylene nonwoven

Measurement	Polypropylene nonwoven	Treatment Position							
		Cover Position		Position 1		Position 2		Position 3	
		(O ₂)	(N ₂)	(O ₂)	(N ₂)	(O ₂)	(N ₂)	(O ₂)	(N ₂)
1	112	97	98	95	110	100	104	103	98
2	110	95	96	100	109	97	102	104	108
3	113	96	102	104	108	99	104	103	110
4	105	98	96	102	104	101	102	95	108
5	111	97	97	103	109	102	101	104	100
6	112	98	98	104	111	99	102	100	107
7	114	97	100	99	103	98	102	105	106
Mean	111.0	96.9	98.1	101	107.7	99.4	102.4	102	105.3
SD.	2.94	1.07	2.19	3.25	3.04	1.72	1.13	3.46	4.50

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Mechanical Properties of PP and PP-PET/C Composites.

1. Mechanical Properties of Polypropylene

Table A 2 Experimental data of Tensile Properties

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	%Elongation at Max Load (%)
1	24.75	384.82	13.6
2	27.58	207.37	18.63
3	21.35	344.53	9.26
4	26.87	345.62	13.15
5	20.48	229.94	12.18
Mean	24.2	302.46	13.37
SD.	2.86	70.31	3.03

Table A 3 Experimental data of Flexural Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Deformation at Max Load (mm)
1	24.75	384.82	13.6
2	27.58	207.37	18.63
3	21.35	344.53	9.26
4	26.87	345.62	13.15
5	20.48	229.94	12.18
Mean	24.2	302.46	13.37
SD.	2.86	70.31	3.03

Table A 4 Experimental data of Impact Strength

Sample	Impact Strength (KJ/m ²)
1	0.37
2	0.74
3	0.36
4	0.38
5	0.67
Mean	0.50
SD.	0.19

2. Mechanical Properties of Unmodified PP-PET/C Composites

Table A 5 Experimental data of Tensile Properties

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	%Elongation at Max Load (%)
1	21.41	367.91	10.06
2	27.18	473.50	26.69
3	23.40	329.18	19.55
4	18.98	208.03	19.20
5	22.45	551.78	18.48
Mean	22.68	386.08	18.80
SD.	2.69	118.63	5.28

Table A 6 Experimental data of Flexural Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Deformation at Max Load (mm)
1	33.42	784.7	10.99
2	34.98	897.2	9.35
3	39.33	896.8	13.39
4	34.51	806.2	11.25
5	34.63	931.0	10.64
Mean	35.57	861.2	11.12
SD.	2.29	61.3	1.46

Table A 7 Experimental data of Impact Strength

Sample	Impact Strength (KJ/m ²)
1	2.37
2	3.21
3	4.67
4	3.33
5	2.74
Mean	3.26
SD.	0.87

3. Mechanical Properties of Oxygen Plasma-modified PP-PET/C Composites

3.1 Cover Position

Table A 8 Experimental data of Tensile Properties

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	%Elongation at Max Load (%)
1	18.51	273.08	8.76
2	31.74	468.61	10.24
3	27.24	330.17	17.54
4	29.32	313.44	14.67
5	26.15	323.98	13.05
Mean	26.55	341.86	12.90
SD.	4.97	74.26	3.53

Table A 9 Experimental data of Flexural Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Deformation at Max Load (mm)
1	38.88	1056.0	11.56
2	40.70	1044.0	11.44
3	40.25	1119.0	12.86
4	41.84	1225.0	11.60
5	34.47	888.2	11.63
Mean	39.23	1067.0	11.82
SD.	2.86	122.6	0.58

Table A 10 Experimental data of Impact Strength

Sample	Impact Strength (KJ/m ²)
1	7.56
2	7.28
3	8.23
4	11.43
5	9.09
Mean	8.72
SD.	1.67

3.2 Position 1

Table A 11 Experimental data of Tensile Properties

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	%Elongation at Max Load (%)
1	21.08	289.10	12.41
2	28.30	498.00	10.89
3	24.67	407.40	11.83
4	22.83	424.42	10.73
5	26.40	444.42	12.53
Mean	24.66	412.67	11.68
SD.	2.85	77.01	0.84

Table A 12 Experimental data of Flexural Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Deformation at Max Load (mm)
1	39.09	1020.0	9.08
2	37.45	977.8	8.89
3	38.19	982.1	8.62
4	30.08	653.2	10.45
5	39.75	1037.0	8.43
Mean	36.91	938.0	9.09
SD.	3.91	156.97	0.80

Table A 13 Experimental data of Impact Strength

Sample	Impact Strength (KJ/m ²)
1	8.17
2	7.76
3	6.93
4	7.80
5	7.08
Mean	7.55
SD.	0.52

3.3 Position 2

Table A 14 Experimental data of Tensile Properties

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	%Elongation at Max Load (%)
1	19.17	543.07	7.62
2	27.74	431.13	11.60
3	24.43	260.54	16.65
4	29.06	284.54	18.08
5	28.14	386.91	13.28
Mean	25.71	381.24	13.45
SD.	4.05	114.71	4.16

Table A 15 Experimental data of Flexural Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Deformation at Max Load (mm)
1	34.76	1002.0	8.97
2	35.24	922.6	8.55
3	33.45	835.7	10.60
4	36.18	899.5	8.20
5	37.21	921.6	9.23
Mean	35.37	916.28	9.11
SD.	1.43	59.56	0.92

Table A 16 Experimental data of Impact Strength

Sample	Impact Strength (KJ/m ²)
1	8.54
2	7.44
3	9.30
4	8.01
5	8.89
Mean	8.44
SD.	0.73

3.3 Position 3

Table A 17 Experimental data of Tensile Properties

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	%Elongation at Max Load (%)
1	23.59	467.64	9.91
2	24.27	306.82	12.23
3	29.03	533.86	17.48
4	28.58	444.35	11.54
5	26.39	246.24	16.95
Mean	26.37	399.78	13.62
SD.	2.45	119.15	3.39

Table A 18 Experimental data of Flexural Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Deformation at Max Load (mm)
1	35.48	838.50	9.17
2	34.54	814.10	8.71
3	37.22	945.00	9.04
4	37.47	990.30	8.43
5	35.07	962.10	9.41
Mean	35.96	904.00	8.95
SD.	1.31	78.58	0.39

Table A 19 Experimental data of Impact Strength

Sample	Impact Strength (KJ/m ²)
1	6.86
2	8.99
3	8.67
4	9.52
5	6.72
Mean	8.15
SD.	1.28

4. Mechanical Properties of Nitrogen Plasma-modified PP-PET/C Composites

4.1 Cover Position

Table A 20 Experimental data of Tensile Properties

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	%Elongation at Max Load (%)
1	17.34	284.62	12.36
2	25.48	441.44	12.99
3	23.53	434.50	10.31
4	24.14	364.17	16.53
5	23.98	504.13	10.27
Mean	22.90	405.77	12.49
SD.	2.85	75.07	2.29

Table A 21 Experimental data of Flexural Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Deformation at Max Load (mm)
1	17.87	560.5	8.09
2	22.02	1122	4.04
3	15.5	795.4	4.12
4	38.22	1455	6.52
5	37.93	1295	10.26
Mean	26.31	1046	6.607
SD.	10.99	365.2	2.66

Table A 22 Experimental data of Impact Strength

Sample	Impact Strength (KJ/m ²)
1	7.66
2	6.61
3	5.65
4	5.63
5	5.38
Mean	6.19
SD.	0.95

4.2 Position 1

Table A 23 Experimental data of Tensile Properties

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	%Elongation at Max Load (%)
1	18.83	549.25	10.07
2	23.58	399.70	11.21
3	18.23	280.92	10.35
4	22.61	551.63	11.40
5	21.76	641.14	11.50
Mean	20.10	484.53	10.91
SD.	2.11	127.96	0.58

Table A 24 Experimental data of Flexural Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Deformation at Max Load (mm)
1	33.75	991.9	8.93
2	41.45	1374	11.44
3	31.32	825.3	12.32
4	37.16	1045	8.66
5	41.29	1282	9.54
Mean	36.99	1104	10.18
SD.	4.5	222.9	1.62

Table A 25 Experimental data of Impact Strength

Sample	Impact Strength (KJ/m ²)
1	4.96
2	7.99
3	6.82
4	6.8
5	7.76
Mean	6.87
SD.	1.19

4.3 Position 2

Table A 26 Experimental data of Tensile Properties

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	%Elongation at Max Load (%)
1	24.43	407.03	11.19
2	23.17	672.07	9.46
3	18.79	512.66	11.63
4	15.51	180.25	13.02
5	22.99	468.25	9.21
Mean	20.98	448.05	10.90
SD.	3.33	160.10	1.42

Table A 27 Experimental data of Flexural Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Deformation at Max Load (mm)
1	27.57	800.5	8.32
2	36.53	1290	9.23
3	18.21	570.4	6.49
4	24.95	1072	5.42
5	36.48	1224	8.97
Mean	28.75	991.4	7.68
SD.	7.86	301.5	1.66

Table A 28 Experimental data of Impact Strength

Sample	Impact Strength (KJ/m ²)
1	5.45
2	5.61
3	4.72
4	5.12
5	5.21
Mean	5.22
SD.	0.34

4.4 Position 3

Table A 29 Experimental data of Tensile Properties

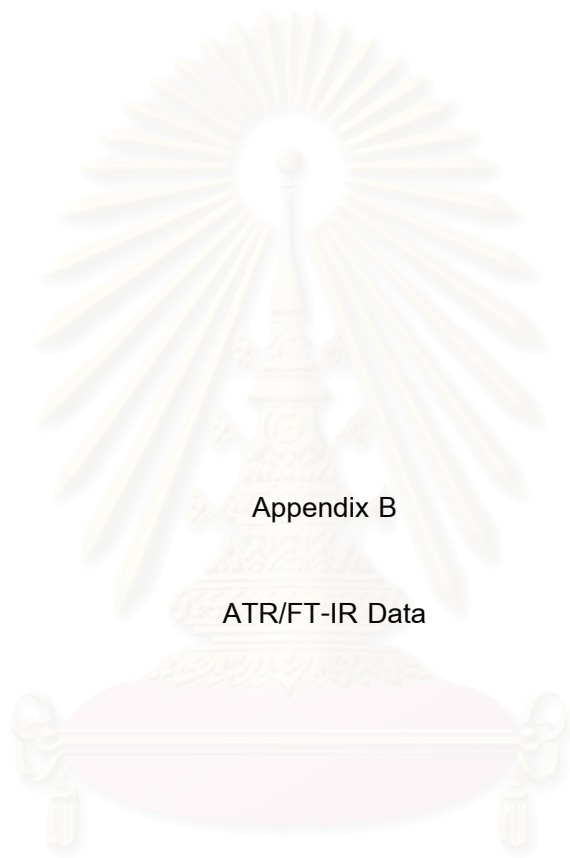
Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	%Elongation at Max Load (%)
1	23.58	349.65	12.30
2	25.73	426.10	11.96
3	26.26	521.82	9.58
4	26.32	522.30	10.80
5	25.96	503.60	10.46
Mean	25.57	464.70	11.02
SD.	1.02	67.56	1.00

Table A 30 Experimental data of Flexural Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Deformation at Max Load (mm)
1	28.87	842.8	10.57
2	26.65	798.3	9.42
3	35.08	1173	10.07
4	33.74	1128	8.2
5	25.47	756.3	9.35
Mean	29.96	939.7	9.52
SD.	4.27	195.60	0.89

Table A 31 Experimental data of Impact Strength

Sample	Impact Strength (KJ/m ²)
1	7.58
2	6.64
3	6.37
4	6.45
5	6.93
Mean	6.79
SD.	0.49

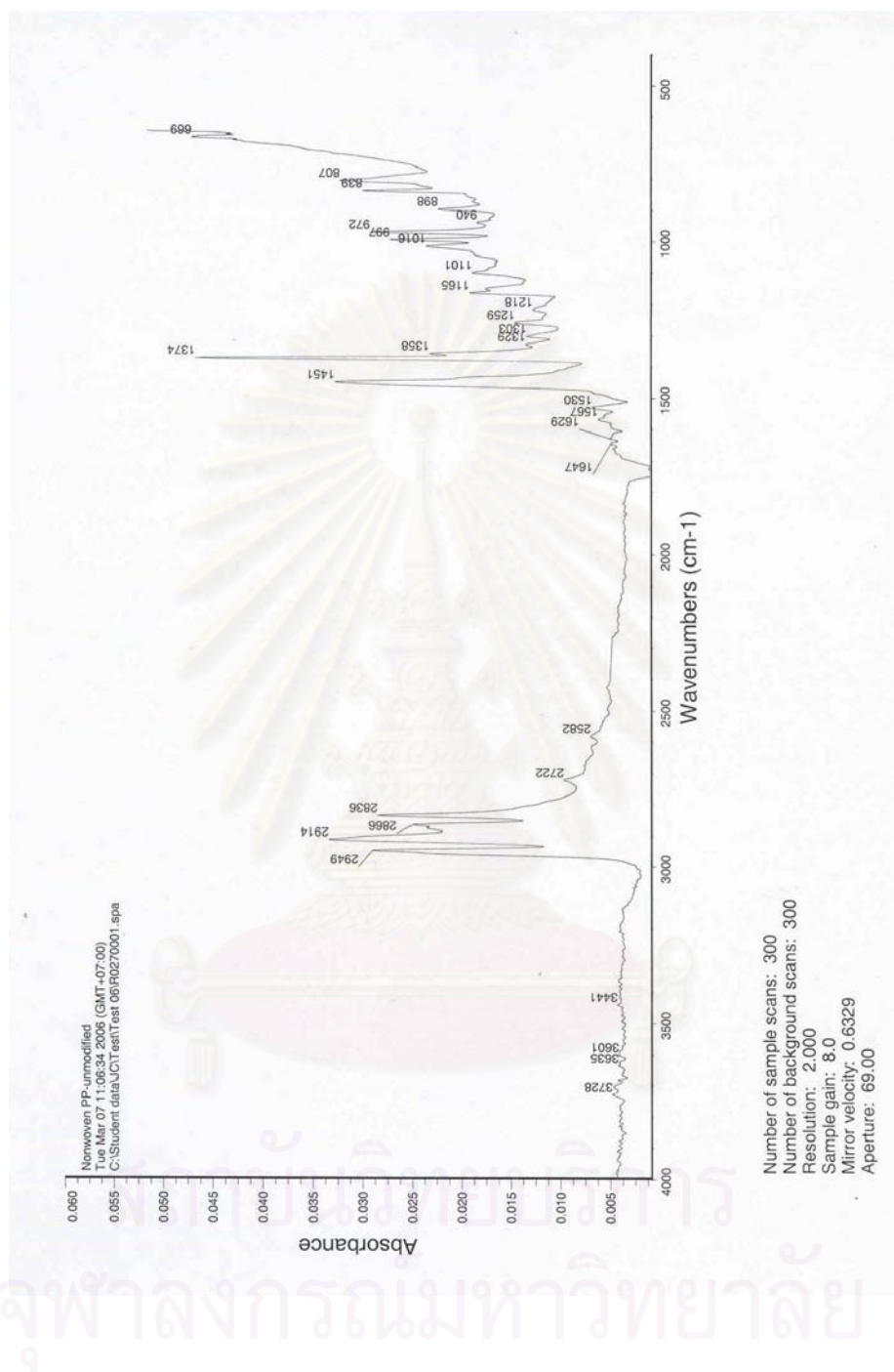


Appendix B

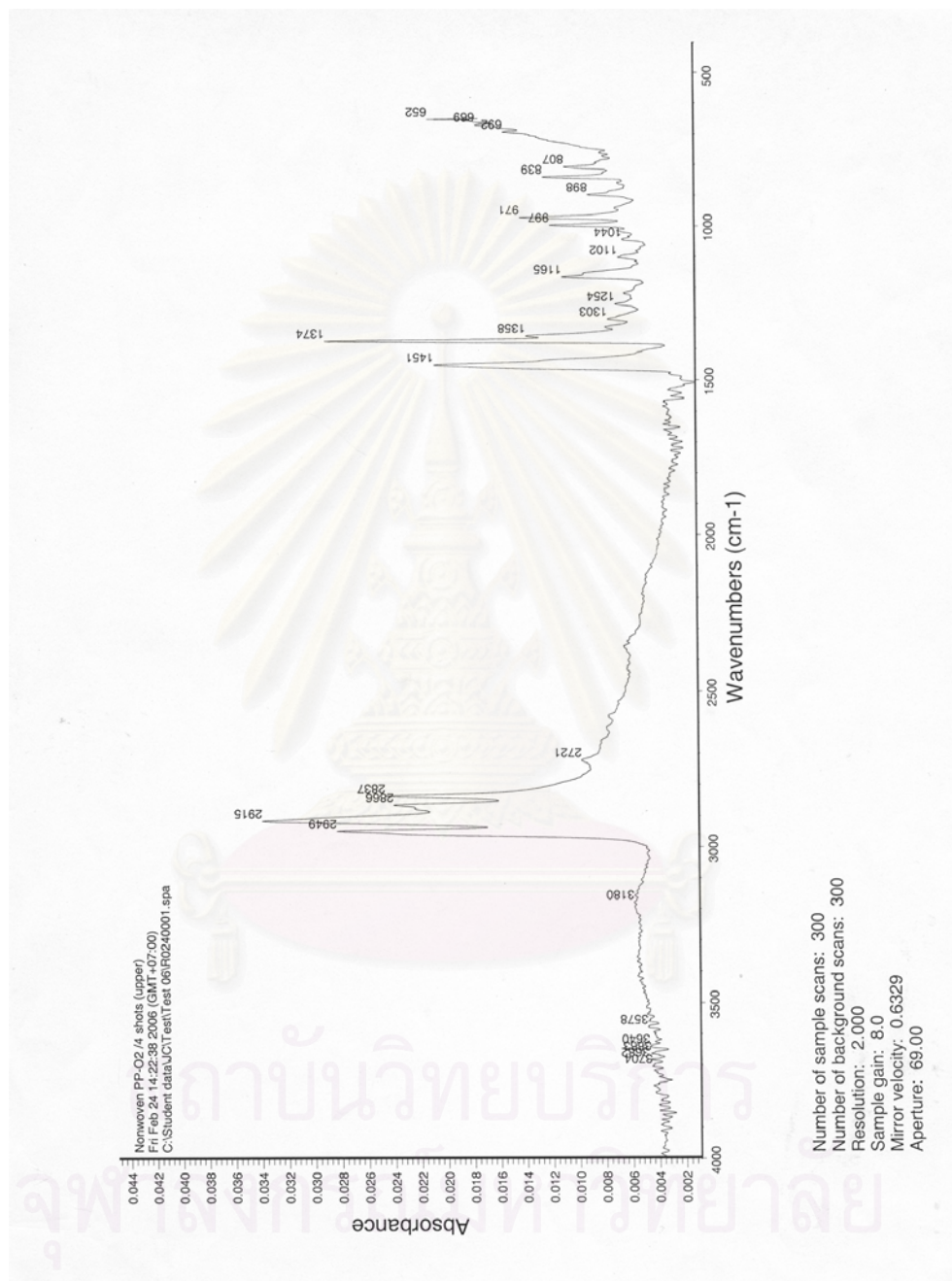
ATR/FT-IR Data

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

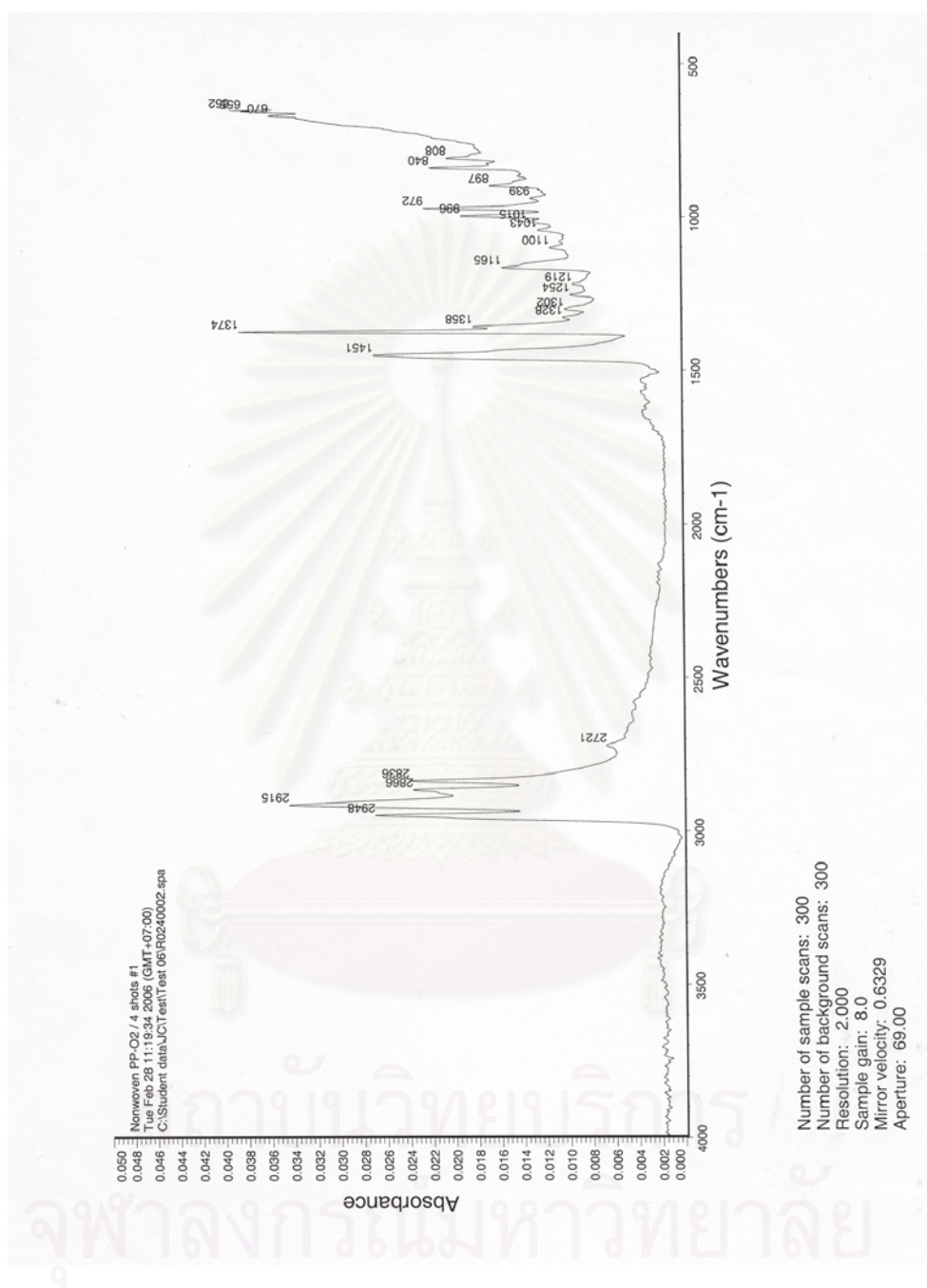
ATR/FT-IR Spectrum of Unmodified Polypropylene Nonwoven



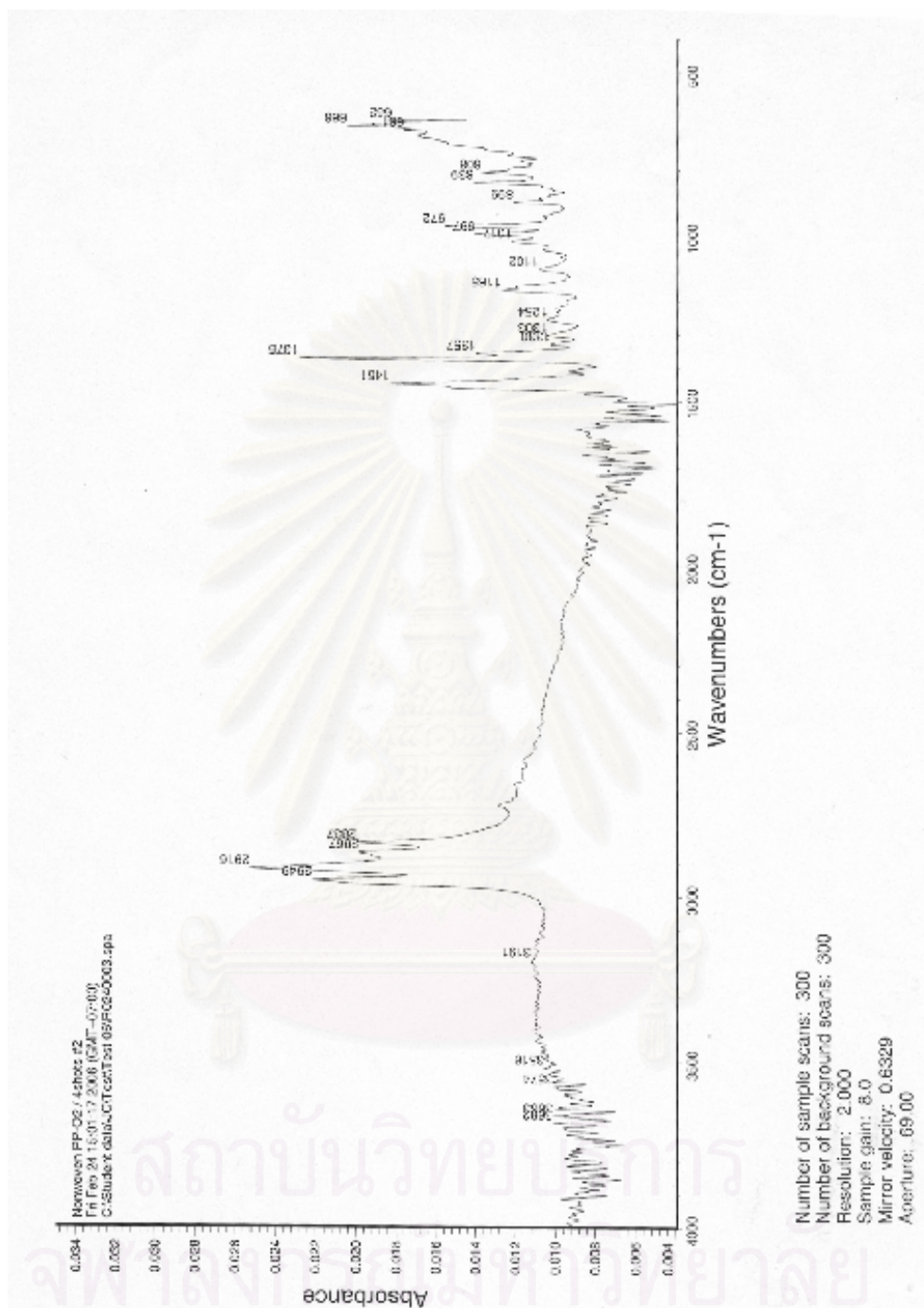
ATR/FT-IR Spectrum of Polypropylene Nonwoven Surface-modified by Oxygen Plasma at Cover Position



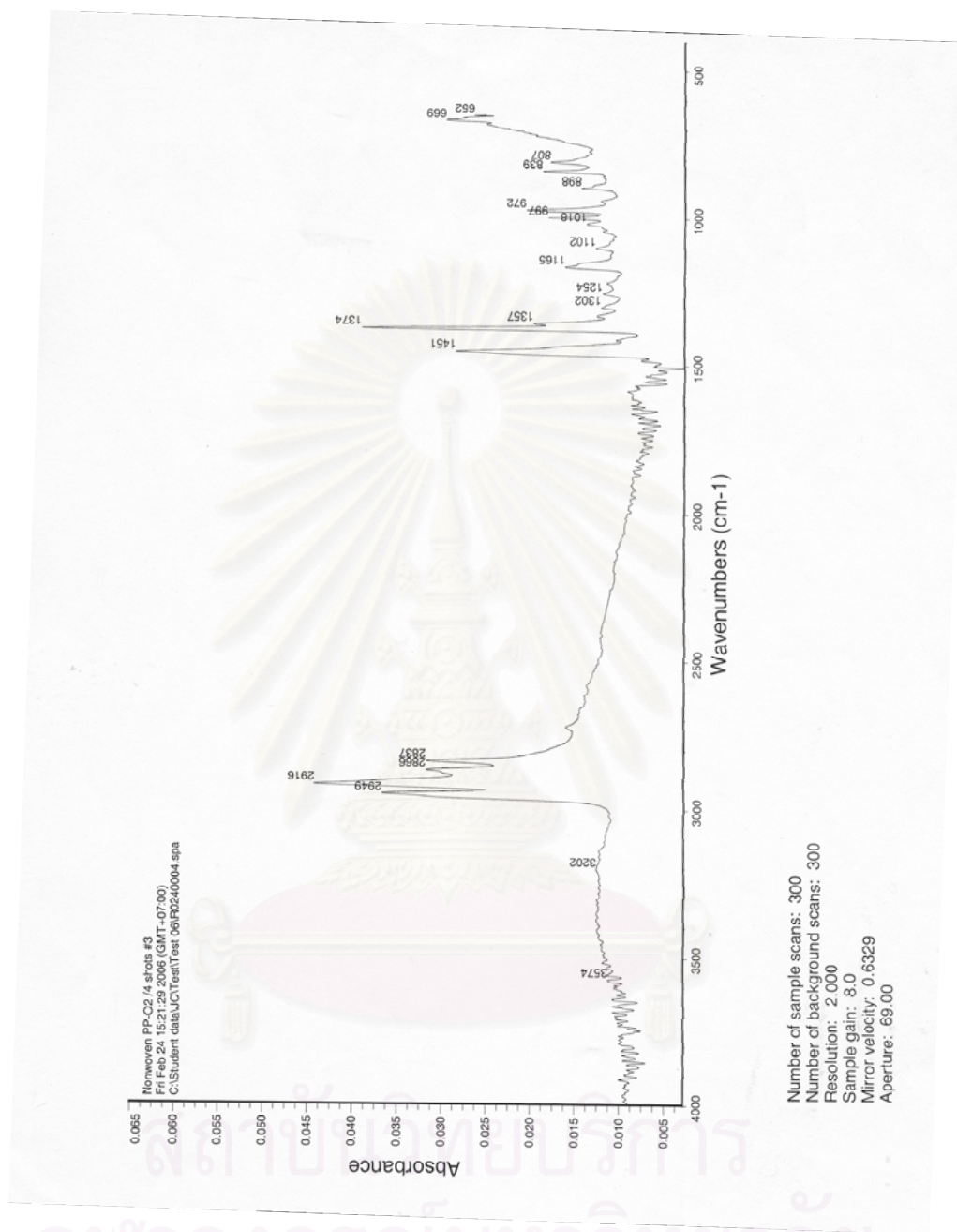
ATR/FT-IR Spectrum of Polypropylene Nonwoven Surface-modified by Oxygen Plasma at Position 1



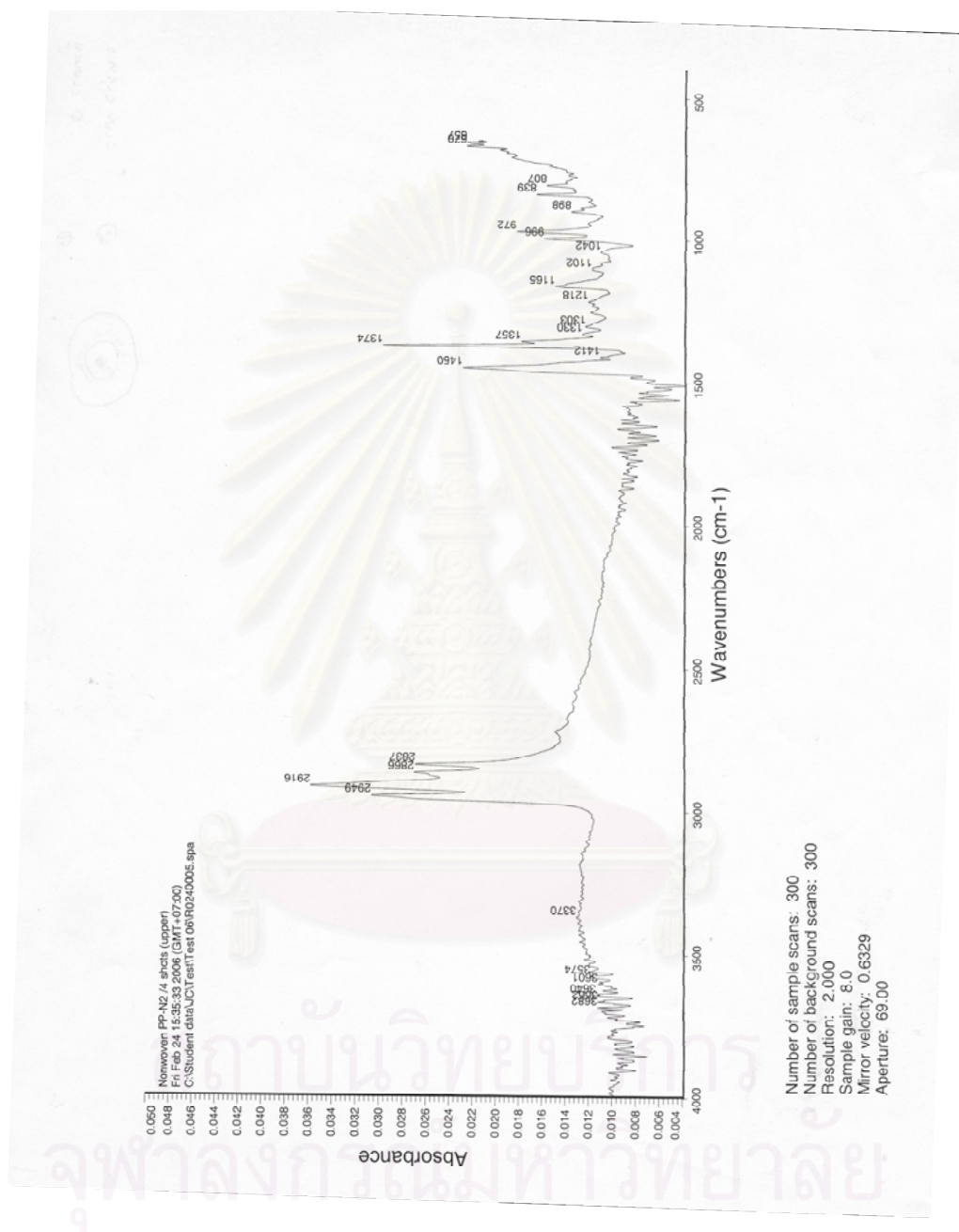
ATR/FT-IR Spectrum of Polypropylene Nonwoven Surface-modified by Oxygen Plasma at Position 2



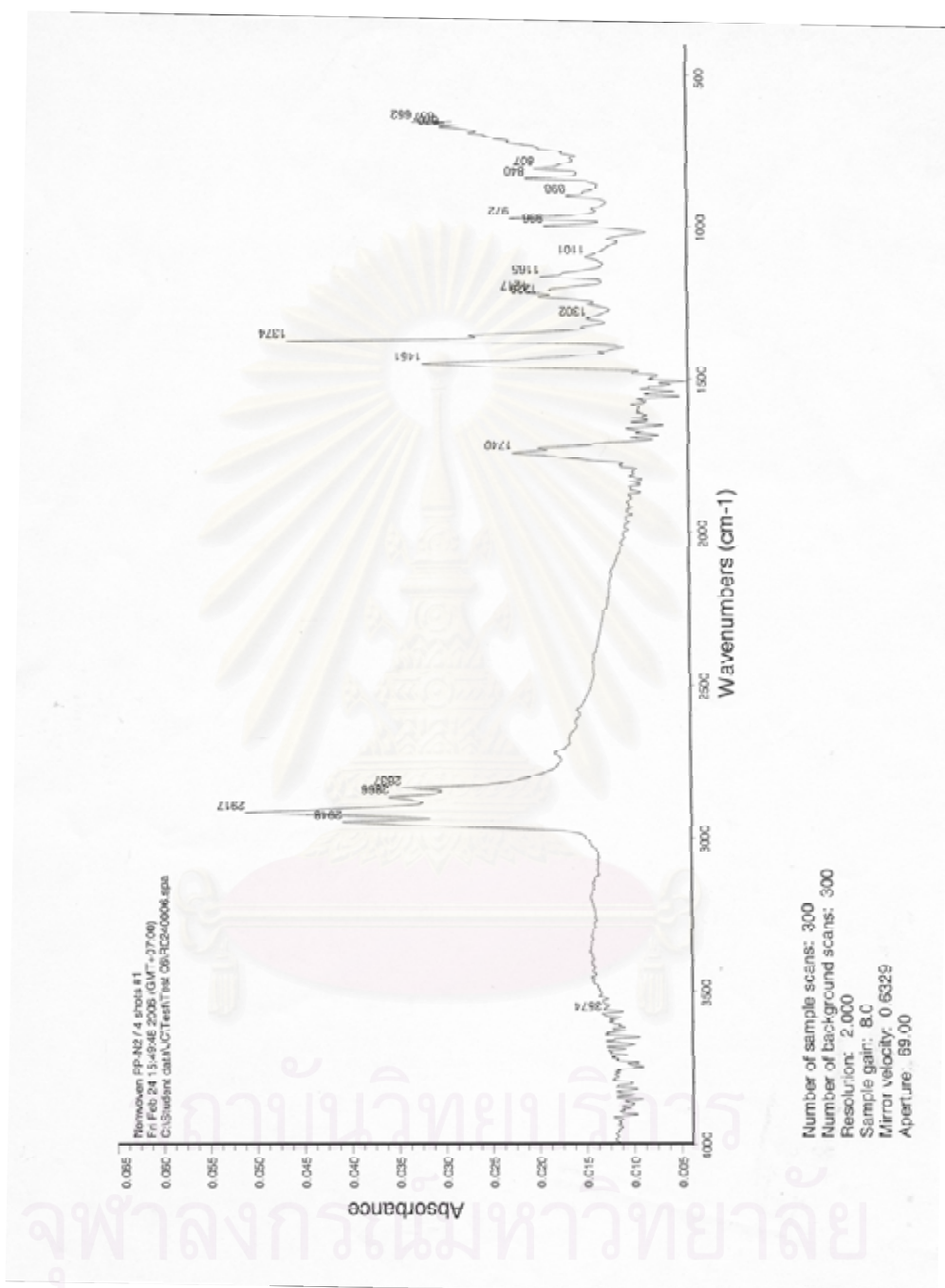
ATR/FT-IR Spectrum of Polypropylene Nonwoven Surface-modified by Oxygen Plasma at Position 3



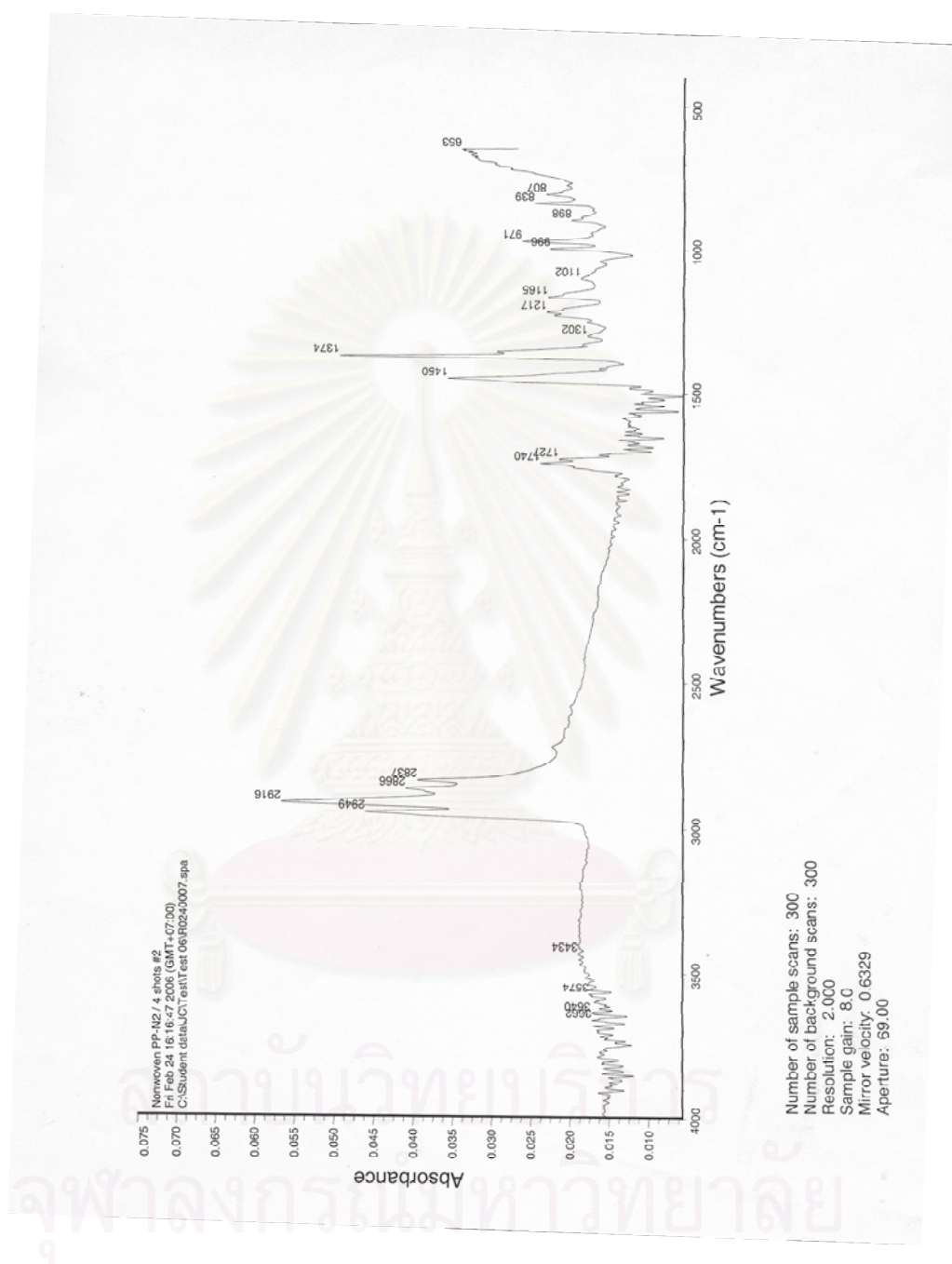
ATR/FT-IR Spectrum of Polypropylene Nonwoven Surface-modified by Nitrogen Plasma at Cover Position



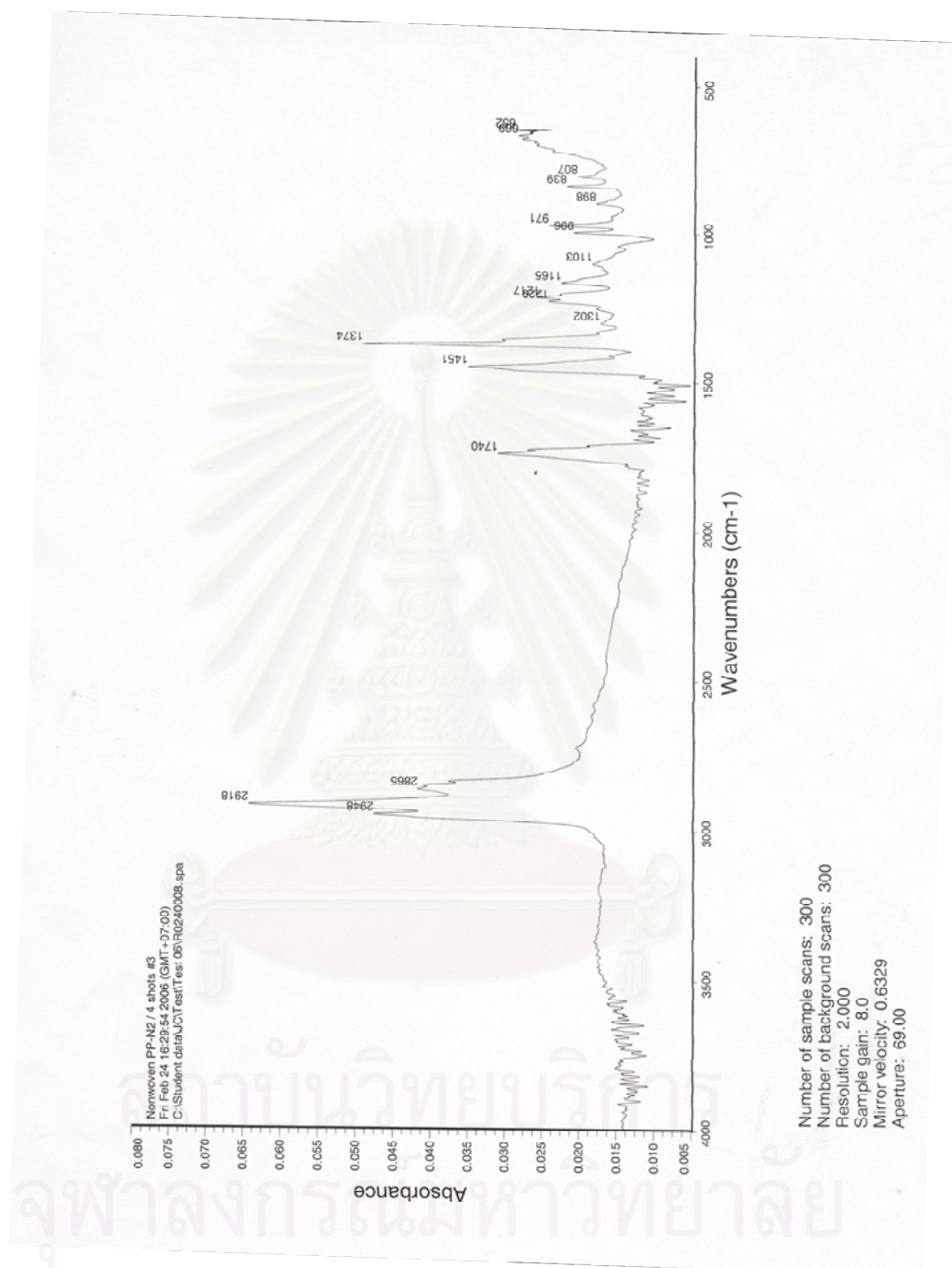
ATR/FT-IR Spectrum of Polypropylene Nonwoven Surface-modified by Nitrogen Plasma at Position 1



ATR/FT-IR Spectrum of Polypropylene Nonwoven Surface-modified by Nitrogen Plasma at Position 2



ATR/FT-IR Spectrum of Polypropylene Nonwoven Surface-modified by Nitrogen Plasma at Position 3



BIOGRAPHY

Mr. Pissanu Jumpa was born in Uttaradit, Thailand on January 13 1982. He received the Degree of Bachelor of Petrochemical and Polymeric Materials, Faculty of Engineering and Industrial Technology, Silpakorn University in 2004. Then, he continued his post graduate study in Applied Polymer Science and Textile Technology Major at the Department of Materials Science, Faculty of Science, Chulalongkorn University and ultimately completed the Degree of Master of Science in Applied Polymer Science and Textile Technology in May 2006.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย