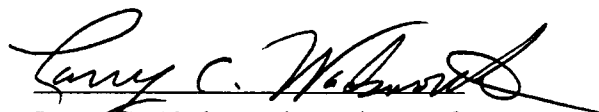
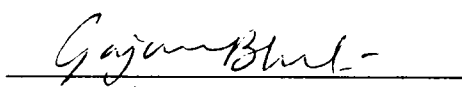
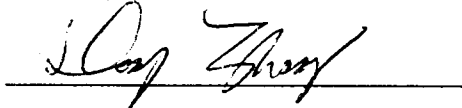


To the Graduate Council:

I am submitting herewith a thesis by Rongguo Zhao entitled "Surface Modifications of Poly(ethylene terephthalate) and Polypropylene Spunbond Nonwoven Webs by Near Atmosphere Plasma Treatment." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a concentration in Textile Science.


Larry C. Wadsworth, Major Professor

We have read this thesis and
recommend its acceptance:


Accepted for the Council:


Associate Vice Chancellor and
Dean of the Graduate School

**SURFACE MODIFICATIONS OF
POLY (ETHYLENE TEREPHTHALATE) AND POLY PROPYLENE
SPUNBOND NONWOVEN WEBS BY NEAR ATMOSPHERE
PLASMA TREATMENT**

A
Thesis
Presented for the
Master of Science Degree
The University of Tennessee, Knoxville

Rongguo Zhao

May 1998

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DEDICATION

This thesis is dedicated to my wife

Mrs. Xinmin Zhao

(趙欣敏 女士)

who has been encouraging and supporting me in many ways
through the international calls

and

to my parents

Mr. Rubin Zhao and Mrs. Xiuling Sun

(趙汝彬先生 和 孫香玲女士)

who have given me invaluable educational opportunities.

ACKNOWLEDGMENT

I am grateful for having the opportunity to study at The University of Tennessee, Knoxville, which has enriched my life. I am most fortunate to finish my Master Degree in Textile Science under the guidance of Dr. Larry C. Wadsworth. Also, the people in the Department of Consumer and Industry Services Management have been very friendly and supportive. I am particularly thankful to my thesis committee, Dr. Larry C. Wadsworth, Dr. Kermit E Duckett, Dr. Gajanan S Bhat, Dr. Dong Zhang and Dr. Qin Sun for their guidance and help in many ways.

There are many other people whose assistance should be recognized. The assistance from Dr. Paul Spence at TANDEC and Dr. J. Reece Roth, who treated all samples using different plasmas, Dr. Charles Yong and Dr. Xiaohong Gu at the University of Georgia, Athens, who helped me in performing the FTIR spectroscopy, Ms. Natalia Castillo, who helped in performing Scanning Electron Microscopy, and Ms. Terezie Zapletalova, who helped in color measurement, are highly appreciated. Also, I would like to thank Dr. Randy Bresee for several helpful discussions. The friendship from professors and graduate students in the Department of Textile Science is recognized in particular. May it last forever.

Finally, I would like to thank the Agricultural Experiment Station, Institute of Agriculture, The University of Tennessee, Knoxville for their generous financial support of my studies.

ABSTRACT

One of the objectives of this project is to improve the dyeability of PET and PP spunbond (SB) nonwoven webs by plasma treatment in order to develop environmentally friendly dyeing process.

Because of the nature of chemical inertness and its super molecular structure, PET fibers are almost only colored by disperse dyeing. This technique usually produces more wastewater carrying disperse dyes, carriers and other potentially hazardous chemicals, which must be purified before being discharged into the environment. There is no effective way to color PP fiber by conventional dyes. Surface modification of these hydrophobic fibers has proven very important to reach this goal.

Spunbond PET nonwoven webs were treated by (SO_2+O_2) plasma and ($\text{N}_2+\text{H}_2+\text{He}$) plasma. The effects of plasma treatment on the dyeability were studied by colorimetry and DSC analysis. Surface characterizations such as optical microscopy, scanning electron microscopy, and Fourier Transition Infrared spectroscopy (FTIR) were conducted.

The research results showed that the dyeability of PET and PP SB webs was significantly improved by plasma treatment. Functional groups were introduced onto the fiber surface and crystallinity was increased with the plasma treatment time. Functional groups played the predominant role in improving dyeability even though the increased crystallinity potentially reduced this improvement. It was concluded that (SO_2+O_2) plasma and ($\text{N}_2+\text{H}_2+\text{He}$) plasma could make the PET and PP SB nonwoven webs easily colored by conventional water-soluble acid dye, which is more environmentally friendly. The (SO_2+O_2) plasma treated fiber demonstrated a "Skin-Core" type structure. The "Skin" is a polarized layer with many functional groups, which is approximately 1.8 microns in thickness. The "Core" is the inner of fiber without plasma affect. The "Skin" layer is the key in improving the dyeability of hydrophobic fibers. Surface chemical changes after oxygen-containing plasma treatment were detected by the means of FTIR.

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I. INTRODUCTION

Poly[ethylene terephthalate] (PET) and polypropylene (PP) are the world's leading synthetic fibers due to their good strength, abrasion resistance, resiliency and low cost. According to McIntyre, Wishman and Hagler [1], the annual productions of PET and PP around the world are over 5.08 million tons and 51.12 million tons, respectively. The PET production in the United States alone is annually 1.5 million tons [2]. They are broadly used in many industrial and hundreds of everyday products, from luxury automobiles to familiar tea bags. Polyethylene (PE) is also one of the most important synthetic polymers. It is mainly used in thin plastic film industry and nonwovens industry. PE has wonderful linear molecular structure and this has been taken advantage to develop high performance fibers [3~6]. PE has the properties of very high crystallinity, high draw ratio, high strength and high modulus. However, the hydrophobic properties of PET, PP and PE make these fibers very difficult to dye with water-soluble dyes. There is no effective way to dye PP fiber except adding pigments to the resin prior to extrusion and melt spinning.

PET fabrics must be dyed with disperse dyes above atmospheric pressure and at relatively high temperature [7]. Otherwise, organic compounds known as carriers, which can potentially pollute air and water, are required. Therefore, water and air pollution remains a great environmental problem, even with all the progress that has been made towards minimizing pollution in recent years.

Based on the understanding of the dyeing principles of hydrophilic fabrics, scientists have been trying to improve the dyeability of hydrophobic fabrics by plasma

treatments, opening a new field that deals with the surface properties of solid polymers. Plasma treatment has been shown to have great potential for improving the wettability, adhesion, printability and the dyeability of textiles. The bright future of plasma technology is a challenge for the fields of materials science, textiles and nonwovens industry, chemical and plasma engineering, advertisement, microelectronic and many other industries. The environmental benefits and energy savings that can hopefully be realized in food packaging, consumer and industrial products, textiles and advertising industries will promote this technique to be the most important technique in the 21st century.

Rakowski [8] published an excellent paper, which compared energy required to improve the dyeability of woolen cloth using a conventional chlorination process with an equally effective low-pressure plasma treatment. He found that as compared to the conventional chlorination process the low pressure plasma modification of 120 tons/year of wool saves 27000 m³ of water, 44 tons of sodium hypochlorite, 16 tons of sodium bisulfite, 11 tons of sulfuric acid and 684 MWH of electrical energy. Furthermore, when used in conventional process, these chemicals produce unwanted or toxic waste products and cause possible occupational hazards to workers.

II. LITERATURE REVIEW

AND RESEARCH OBJECTIVES

1. Structural properties and dyeability of polypropylene (PP) and poly[ethylene terephthalate] (PET) fibers

The dyeability of fibers is controlled by their chemical properties as well as physical properties. Chemically, fibers that have polar functional groups in their molecular repeat units are more easily dyed. The polar groups serve as active sites for attraction of dye molecules. For example, in cotton, the hydroxyl groups (—OH) are strong polar functional groups, which make cotton hydrophilic. When cotton fibers are submerged into an aqueous dye solution, they adsorb dye as well as water molecules. Under suitable dyeing conditions, cotton fibers will become swollen, which facilitates dye molecules to diffuse into the inner regions of cotton fibers. Physically, fiber-forming polymers have crystalline and noncrystalline regions in their structures. In the crystal regions, the polymer molecules are arranged orderly and packed tightly, although the crystalline region may not necessarily be oriented in the fiber direction. In the amorphous regions, the polymer molecules are randomly arranged. This allows the dye molecules to penetrate into these regions along with the water under a proper condition.

PP molecular chains have no polar functional groups so the dye molecules can not be chemically bonded onto the fiber, or even can not be strongly adsorbed by the

fiber surfaces because of their hydrophobic properties. Therefore, PP fibers are extremely difficult to dye.

Because of only weak polar ester groups (-COOR) in the molecular repeat units, PET fibers are also hydrophobic. On the other hand, because of their high orientation and relatively high crystallinity, PET macromolecules are closely packed, and the high degree of inter-chain bonding result in a high glass transition temperature. Thus PET fibers are relatively inert, chemically, and less penetrable to solvents and dyes [9]. Traditional water-soluble acid and basic dyes cannot be used for dyeing PET fibers because they normally contain no basic or acid groups. Under this situation, disperse dyeing is almost the only technological option for dyeing PET fibers. This technique requires disperse dyes that are basically water insoluble and can be performed only under comparatively high temperature and pressure. It is obvious that it requires more energy to maintain high temperature and pressure. Otherwise, carriers are required to push apart the tightly packed molecular chains in order to promote the penetration of dye molecules into the fibers. This process usually produces more effluent carrying disperse dyes, carriers and other potentially hazardous chemicals, which should be purified before being discharged into the environment.

2. Efforts for improving dyeability of hydrophobic fibers

Researchers have been trying to improve the dyeability of PET fibers for years. Some of them changed the macromolecular structure by introducing small amounts of strong polar monomers into the molecular chain [10]. Some of the additives were added to the fiber-forming polymer prior to extrusion to partially disturb the PET

supermolecular structure [11]. Indeed these methods were helpful to improve PET dyeing properties but at the cost of losing mechanical properties.

Similar approaches, i.e. fiber modification, had been taken to make polypropylene dyeable, which include copolymerization to provide dye-sites along the macromolecular chain and blending with dyeable polymers. Baumann [12] reviewed the attempts by several researchers to improve polypropylene dyeability. The method of grafting chloromethylstyrene was introduced. In addition, the method of blending a polyethyleneimine compound with polypropylene was described briefly. Bromination of polypropylene fibers was reported to give the fibers an affinity to basic dye [13].

In recent years, modifying the surface of hydrophobic fiber by plasma treatment opened up new possibilities in this field. By using special gas plasma treatment or plasma polymerization [14], functional groups can be introduced onto the surfaces of PET and PP fibers. The polar layer on the fiber surface improved the wettability and the affinity of the fiber to dye molecules. After reaction with or attraction by the functional groups, which are introduced by plasma treatment, dye molecules are fixed on the fiber surface. Because plasmas do not interact with the inner part of the fiber, this technique may not greatly influence the mechanical properties of the treated fiber [15].

3. Surface modification of polymeric fibers

Because of the nature that most of synthesized polymers have relatively low surface energy as shown in Table II-1, they have serious problems in wettability,

Table II-1 Critical Surface Tensions of Typical Polymers (20~25°C)

Polymer			Critical Surface Tension (γ_c) [mN m ⁻¹ $\equiv$ dyne cm ⁻¹]
Polybutadiene			31
Polyethylene			28-34
Polyisobutene			27
Poly(propylene-co-ethylene)			28
Polypropylene			29-34
Polyacrylamide			35-40
Polyacrylate (plexiglas)			29
Poly(butyl acrylate)			28
Poly(methyl acrylate)			41
Poly(acrylic acid-co-ethylene)	20.7:79.3	mol%	59
	14.3:85.7		55
	8.2:91.8		44
Poly(ethyl methacrylate)			33-44
Poly(vinyl acetate)			37
Poly(vinyl alcohol)			37
Poly(vinyl chloride)			37
Poly(styrene)			32-35
Poly(ethylene terephthalate)			43
Polyamide			32-42
Kevla			47 $\pm$ 1.5*

Note: Data taken from reference [16]

* This is from reference [17]

printability and adhesion properties, which greatly limits their applications. To improve these surface-related properties, extensive research has been carried out. The methods of polymer surface modification can be classified into the following categories:

- mechanical abrasion
- caustic chemical etching
- wet chemical graft polymerization of polar monomers
- wet chemical polar polymer coating
- plasma induced surface modifications

Modification of polymer surfaces is the most important part in the current project and also the potential key to solve the problems being faced. It is valuable to briefly review these methods in the following sections.

3.1 Mechanical Abrasion and Wet Chemical Etching

It is generally accepted that the higher the specific surface area, the easier the surface adsorbs other materials and the higher the bonding strength. Based on this principle, mechanical abrasion and chemical etching were employed to improve the specific surface areas of synthesized fibers, which have relatively smooth surfaces. It was reported that PET fine fibers were chemically etched by concentrated NaOH solution and rough fiber surfaces were observed which resulted in better moisture regain and deeper color shade [18]. The advantage of these methods is simple in operation. But they are not effective and also have other disadvantages. For fine polymeric materials, such as fine fibers and microspheres, mechanical abrasion would not increase the specific surface area significantly. For brittle materials, the abrasion method could not

work well. Usually, the wet chemical etching process has serious environmental problems. On the other hand, it tends to significantly decrease the mechanical properties of the treated materials.

3.2 Wet Chemical Graft Polymerization of Polar Monomers

Chemical surface grafting polymerization used in modification of polymers represents a practical and widely used technique. The principal problem in this procedure is the synthesis of an initiator site on a solid polymer surface. In the case of chemically inert polymers such as polypropylene, this problem is more acute since the initial polymer has no chemical reactive sites. To create reactive sites, chemical etching, radiation and plasma procedures were employed [21].

The solid polymer with new created reactive sites was treated in a strong polar monomer solution. Under appropriate conditions such as suitable temperature, time and pressure, grafting and polymerization reactions can take place between the active sites and the monomers. As a result of these reactions, a thin polymer layer of different chemical composition covered the original material. Chemical bonds at the interface connected the two different polymers tightly.

3.3 Wet Chemical Polar Polymer Coating

Because of the super chemical resistance of fluoropolymers such as poly(tetrafluoroethylene), it is quite difficult to create reactive sites on their surfaces. Thus the technique of wet chemical graft polymerization does not work well to these kinds of polymers. As an alternative approach, Molly S. Shoichet and coworkers [19]

suggested wet chemical polar polymer coating, which did not need reactive sites on the polymer surfaces. The polar polymer was first dissolved in proper solvent to prepare a solution or paste, and then was adsorbed or coated evenly on the substrate surface. After the solvent was removed by heat, a thin polar layer was created. According to the authors, the surface energy and adhesive properties were significantly improved.

The similar technique was proposed by Zhao [20] in modifying the PET fabrics for anti-static and softening properties. The difference from the above-mentioned process is that the multi-functional, low molecular weight polymers (anti-static agents/softeners) and cross-linking agents were adsorbed onto the fabric surfaces simultaneously. During heat setting stage, cross-linking reactions occurred and a 3-D polymer film was formed on the fabric surfaces.

3.4 Plasma Induced Surface Modifications

3.4.1 Introduction to plasma

The field of plasma engineering has been active since 1960's with the space technology races between USA and former Soviet Union. A huge amount of high tech has been launched commercially in the field of military, metallurgy, tools industry, material science, microelectronics, food decoration, textile and other branches. Extensive researches are being carried out all over the world, which include plasma physics, plasma chemistry, plasma hardware and software. The reason that plasma engineering draws so much attention was mainly from its inherent properties of energy-saving, environmentally friendly properties and effectiveness [21].

Basically, plasma is an electrically neutral collection of active species such as free radicals, ions, electrons, neutral atoms and gas molecules, etc. It can be ignited and sustained by electrons accelerated in an electric field under low pressure, such as 0.1 mmHg (Torr) or lower. The accelerated electrons collide with the gas molecules and transfer energy to them resulting in excited molecules and ions with different charges. The mixture of neutral and charged particles is called plasma.

According to the principle of energy conservation, plasma can acquire enough energy to be used for many kinds of industrial and military purposes. Plasma can be classified into two categories: hot and cold plasma [22-23]. The hot plasma is almost totally ionized, approaching a complete thermodynamic equilibrium, having high energy and high temperatures. These plasmas are used in nuclear industry, in rocket propulsion and laser technologies. The cold plasma is a partially ionized complex mixture of electrons, ions, free radicals, excited atoms and molecules. It is in non-equilibrium with relatively low energy. Except that the electrons are at high temperature, nearly 10^4 K, the other plasma species are at almost ordinary temperatures. The energy of cold plasma falls in the range of 0~20eV, which is strong enough to break almost any chemical bonds, as shown in Table II-2.

In this way, chemical reactions can be carried out which runs only with very low rates in the framework of traditional organic chemistry. However, plasma active species can penetrate only few hundred nanometers into the material surfaces, so this technique can modify the surface properties without significantly altering their bulk properties. For polymer surface modification, only cold plasmas are employed. Because most cold plasma is operated under low pressure (lower than 0.1 Torr), they are sometimes named

Table II-2 Bond Strength of Selected Chemical Bonds [24]

Diatomic	ev	Polyatomic	ev
Al-Al	1.38	NH ₂ -NH ₂	2.62
Al-Cl	5.3	O=CO	5.51
Cl-Cl	2.51	CH ₃ -CH ₃	3.9
C- Cl	4.12	CH ₂ =CH ₂	7.6
F-F	1.63	CH ₃ =CH ₃	10.0
O- Si	8.29	HO ₂ -OCC(CH ₃) ₃	2.0
O- Sn	5.5	CF ₂ =CF ₂	3.31
N-N	9.8	CN-CN	5.56
Si-Si	3.38	CH ₃ -CN	5.28
C-N	7.8	C ₆ H ₅ CH ₂ -NHCH ₃	2.97
C- Si	4.6	CO-Fe(CO) ₄	1.78
C-O	11.16		

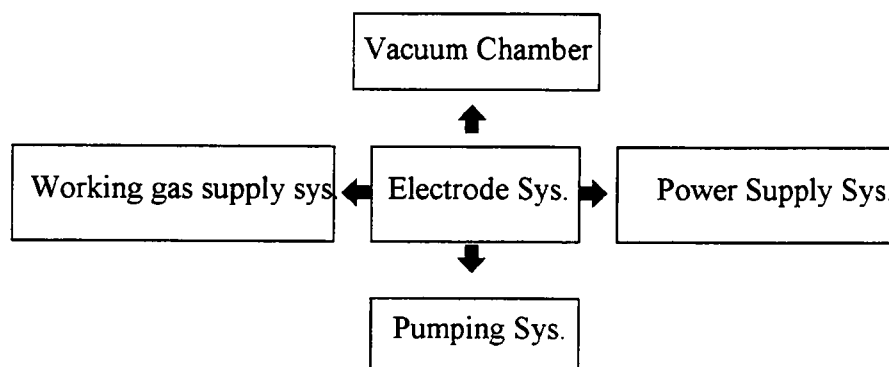
“low pressure plasma.” The low pressure means an expensive vacuum system and batch treatment method, which limited this technique to the research labs or high-tech industries, such as microelectronics. It is obvious that employing this technique in the continuous industrial product lines requires a great amount of money and will face formidable difficulties. For example, the production efficiency would be low because of the batch method, which could not satisfy the industrial requirements of high production efficiency.

The University of Tennessee at Knoxville (UTK) had recently developed “One Atmosphere Plasma” process, which is capable of generating a uniform, steady state glow discharge plasma at one atmosphere in air and/or other working gases [25~30]. It is very convenient for the active species from this plasma to be applied to fabrics as part of a continuous production process. Compared to low pressure plasma, where pressure

is lower than one thousandth atmosphere, one-atmosphere plasma are sometimes called high-pressure plasma. This technique made PET and other hydrophobic fibers such as PP wettable and even rewettable for a considerable length of time. This increased affinity increased the accessibility of the fiber to dyes and finishes, thereby hopefully enabling lower energy processing with less pollution.

3.4.2 Plasma System Configurations

Based upon the operating pressure, plasma systems are classified into two groups: low pressure plasma (a few mTorr to a few Torr), high pressure plasma (tens of Torr to over one atmosphere). For a low pressure plasma system, the major structure components of plasma processing system are shown in the following figure.



- A working gas supply system usually includes sets of high-pressure gas jars, needle valves, gas flowmeter and gas pretreatment elements such as heater and condensation traps.

- The vacuum chamber serves to control the gas amount and gas composition. It also prevents the release of harmful x-ray, UV light and ozone to the operating area. It is the joint of all other plasma systems.
- Electrode system has several configurations, which may or may not be located in the reactor chamber. They are usually in the form of parallel plates or concentric plates to provide uniform electric field between the electrodes. Some kinds of dielectric materials are often employed to coat or cover the electrodes in order to improve the uniformity of the plasma. They also prevent short-circuiting of the system.
- Pumping system consists of pumps with different vacuum capacities, leak valves and high quality pipelines. It is connected to the vacuum chamber to remove the undesirable gases and the harmful chemical byproducts like ozone.
- Power supply system is the energy source of the plasma reactor. It may be a DC or RF power supply. In general, DC power supply is relatively cheaper than RF power supply, but RF power supply interacts with plasma by displacement currents, rather than real currents. This advantage allows the electrodes to isolate with plasma so as to prevent plasma contamination from electrode materials.

A variety of plasma reactor configurations have been described in the literature [23-31]; for example, parallel plate RF plasma reactor configuration, barrel reactor configuration, and downstream microwave plasma reactor configuration. These configurations require an expensive vacuum system and are only operated in a batch processing style. One-atmosphere plasma provided a commercial possibility of continuous processing method without high vacuum chamber. The schematic drawing

of one-atmosphere glow discharge plasma reactor illustrates the main components in this system [32].

3.4.3 Parameters of Plasma Operation

The plasma system is very complicated. Operating pressure, power level and power frequency are the most common variables that have direct relationship with the plasma parameters, such as electron number density, power density and current. To generate an uniform, steady state plasma and control the plasma conditions, attention needs to be given to the following parameters:

- Power level directly relates to the energy of active species. For a RF power supply, high frequency may create high power output.
- Separation between the electrodes may be changed according to the practical requirement. Higher electric field is obtained when the gap distance is reduced and vice-versa. The power density increases with the gap distance.
- System pressure reflects the particle number density at a given temperature and volume. Under relatively high pressure, particle number density is correspondingly high, which results in short mean free paths and lower kinetic energy because of high collision frequency.
- Type of working gas, to some extent, determines the power level that initiates the plasma due to the specific ionization potential of each gas.
- Gas flow rate determines the residence time of the gases in plasma; hence it may affect the active species number density and the interaction with the substrate.

3.4.4 Polymers and Plasma

Polymers have been used everywhere from high-tech space industry to everyday life materials. It is hard to imagine our life even only one day without polymers. The solid polymers are produced in various forms such as films, microspheres, fibers, fabrics and many others. They can be natural polymers like wool and cotton, or synthetic polymers, such as polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET). Many synthetic polymers possess excellent physical and chemical properties, which are determined by their chemical composition, structure and morphology. But they generally have relatively very low surface energy, as shown in Table II-1. It is generally accepted that the communications between two materials mainly occurs on surface, so that their applications, to some degree, are limited because of this poor property.

Plasma used in surface treatment produces active species that are numerous different in kinds and/or energy. These active species interact with the solid polymer surfaces to greatly change the surface energy, wettability, printability, adhesion and other commercially important surface properties. Under suitable plasma conditions, these active species can also induce surface polymerization, cross-linking of molecular chains and scissoring of molecules as well as introducing new functional groups on the polymer surfaces. Many techniques have been reported or patented to perform plasma treatments, which include corona and glow discharges, for instance, DC glow discharge, RF glow discharge and MW glow discharge.

3.4.5 Plasma Surface Functionalization Using Suitable Working Gases

In the glow discharge process, an electric field is applied on a gas and free electrons are accelerated by the electric field. They gain energy and collide with neutral molecules in the gas, transferring energy. The interaction between electrons and neutral molecules causes ionization, dissociation, excitation and electron exchanges, which create active species such as ions, excited molecules as well as free radicals.

Many gases and gaseous mixtures, for example, argon, nitrogen, nitrogen/hydrogen, oxygen, nitrous oxide, air, ammonia, have been employed as plasma working gases for different purposes. The most frequently reported working gases were oxygen and ammonia. In Table II-3 it is shown that many polymer materials were treated by plasma techniques and different functional groups were detected.

Although a lot of work has been done by the scientists all over the world, the mechanism of introducing functional groups is still not clearly understood in detail. However, it is obvious that implanted functional groups definitely relates to the type of working gases and other operating parameters. Empirically, the functional groups have the following relationship with the types of working gases:

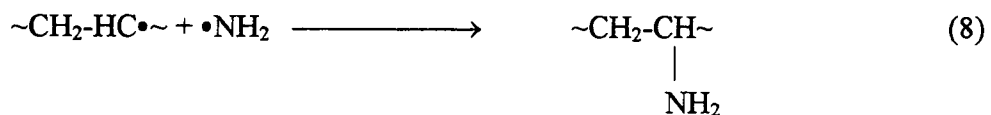
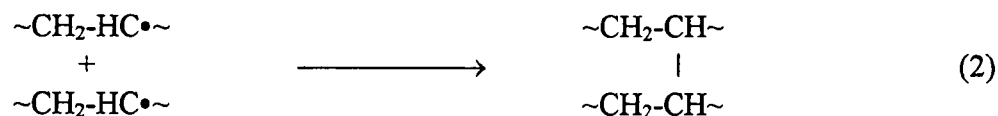
CO and/or CO ₂	—————→	--COOH, --CO--
O ₂ /air	—————→	--OH, --COOH, ----CO--
N ₂ / NH ₃ , NO, N ₂ O, NO ₂	—————→	--NH ₂ -- , --NH--[7], -NO ₂

If the polyethylene is taken as the example polymer and ammonia as the example of working gas, the following figure in some degree shows the complex of possible reaction [48,49]:



Table II-3 Polymer Surface Modification by Plasma Treatment

Materials	Plasma Type	Functional Groups	Research Purposes	References
Polystyrene polyethylene	Argon	carbonyl groups		[33]
polystyrene polyethylene polypropylene	Nitrogen	nitrile s, amines imides/ amides		[34]
	Nitrogen/ Hydrogen	amino groups		[35]
poly(vinyl chloride)	Ammonia			[35]
polyethylene fiber	oxygen		increase in adhesion due to enhanced mechanical no decrease in tensile strength	[36]
PET tire cord	Ammonia		increase in wettability and bonding strength	[36,37]
Kevla fiber	Ammonia	amine groups	increase in peel strength fabrics	[38]
Aramid fiber	Ammonia	amine groups Nitrogen	increase in fiber/matrix (epoxy)interfacial bond strength	[39]
Extended chain PE fiber	Ammonia	amine group	stronger fiber/matrix(epoxy) increase in interlaminar fracture energy and shear strength	[40-43]
Wool and PET fabrics	Helium/Argon Acetone/Argon Oxygen	-CO- -COO-	considerably improved wettability & surface tension & printability	[44-45]
Polyamide	Argon	-CO- -COO-	increase in the depth of shade of black dyed poly- amide fabrics	[46]
Cotton	Ammonia	amide groups activated carbonyls	improvement in dry wrinkle recovery	[47]



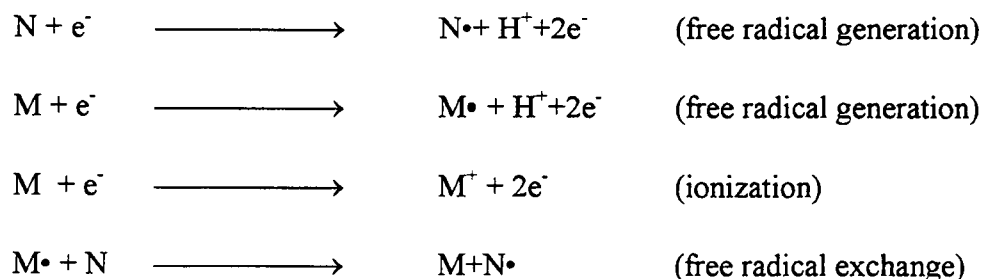
Various kinds of reactions can occur between these active species by collisions and energy transfer. For example, surface macromolecule cross-linking (reaction 2), chain scission (reaction 3), ionization (reaction 5) and grafting (reaction 8).

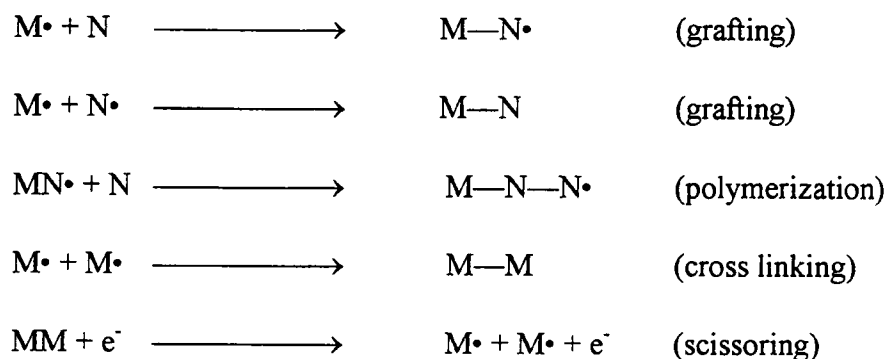
Under suitable conditions, the mixture of two or more kinds of gases is required to acquire better treatment results. In the UTK textile research lab, the mixtures of (CO₂+O₂) and (N₂+NO) [50] had been employed during surface modification of PET fiber by atmospheric plasma treatment. The results showed that samples treated with (CO₂+O₂) had good affinity to basic dyes and samples treated with (N₂+NO) exhibit good dyeability to acid dyes. These preliminary results suggested that acidic functional groups, such as COOH and --OH, were introduced onto the fiber surface when the working gas was the mixture of (CO₂+O₂). They also suggested the basic functional groups when working gases were N₂ and NO.

Oxygen and ammonia plasmas have been frequently employed to modify the surface of various fiber and fabrics. Functionalities of primary amines were analyzed by chemical method [38,43] as well as ESCA. Majid Sarmadi, and co-workers [2] used SiCl_4 plasma to treat PET fibers. The functional groups $\text{Si}(\text{OH})_x$ were produced, which promoted the wettability and the dyeability of PET fabrics.

3.4.6 plasma induced polymerization of polar monomers

During plasma treatment, the proper monomer and/or working gas were introduced into the reactor chamber, active species from the plasma interacted with the monomer and the substrate. Complicated reactions took place simultaneously. Researchers have suggested several mechanisms to build suitable model to explain the experiment results [48, 49, 51.]. Generally speaking, free radicals produced by the interaction of plasma with monomer/working gas/ substrate play a critical role during the polymerization. Because the free radicals are very reactive, the ionic initiation and propagation may coexist and polymerization takes place in gas phase as well as on the substrate surface [52]. The principal reactions are shown as follows:





where M denotes the substrate polymer macromolecules, N is the neutral monomer and working gas molecules, $M\bullet$ and $N\bullet$ are free radicals. The final results are influenced by many factors such as power level, gas type, gas flow rate, monomer properties, temperature and treatment time, etc. It is difficult to tell which reaction is dominant or which one is more active. Polymer produced on the surface connects the substrate by chemical bonds. Different forms of polymer may be created on the substrate surfaces, which depend on the plasma practical parameters, for example, pressure and flow rate. Research results have shown that higher monomer flow rate and lower pressure are suitable for developing solid thin films, whereas lower monomer flow rate and higher pressure are mostly suitable to yield polymer powders [52]. These plasma-derived polymers are extremely irregular, highly cross-linked and totally amorphous in nature [51,53]. The functional groups are partially maintained in the surface polymer. Some other functional groups are also observed, although they may not exist in monomers, for example, carbonyl ($>C=O$) and ether groups ($-O-$), which is mainly a result of residual air in the plasma chamber.

Oxygen-containing functional groups are among the most effective hydrophilic groups. But ordinary alcohols, aldehydes and esters were scarcely employed as

monomers because they do not produce hydrophilic polymer films. The reason of this phenomenon was probably the fragmentation of these molecules at the oxygen atom sites. Kikuko and co-workers [54] recently found that propargyl alcohol ($\text{CH}\equiv\text{C}-\text{CH}_2\text{OH}$) conducted plasma polymerization under very low electric power condition by which the fragmentation at the oxygen atom sites could be minimized. They produced polymer films with high wettability and transparency. They also surveyed eight other oxygen-containing organic monomers, mostly unsaturated, and concluded that alcohols having triple bonds were the most practicable monomers for preparation of hydrophilic polymer films by the plasma polymerization techniques. They supposed that the triple bonds caused polymerization with soft plasma condition which resulted in least damage to the hydroxyl groups ($-\text{OH}$).

Other organic compounds had also been tested as monomers for plasma polymerization. These chemicals usually were unsaturated nitrogen/sulfur-containing compounds, such as allylamine ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_2$) [55] and 1-benzothiophene [56]. The plasma polymerization conditions were quite different between oxygen-containing and nitrogen/sulfur-containing monomers. The reasons could relate to the chemical nature of the monomer but not well documented in literature.

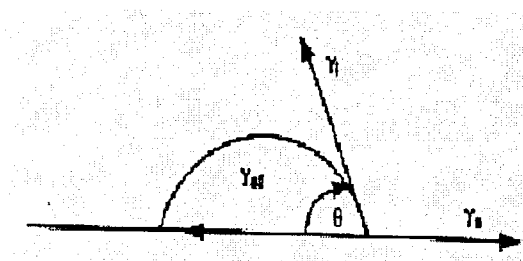
Plasma reduced graft polymerization of polar monomers had been used to prepare reverse osmosis membranes [57] and surface modification of high performance fibers such as glass fiber [58], aramide fibers [59] and ultra-high-strength polyethylene fibers [55]. This method was also employed in modification of polyurethanes (PUs) in order to improve their blood compatibility [54].

4. Techniques For Surface Characterization

4.1 Dyne solution test and contact angle test

It is well known that the surface energy determines most of surface properties of the polymeric materials, such as printability, wettability and adhesion properties. Unfortunately it is very difficult to measure the polymer surface energy. Actually the most frequently measured is wetting tension, which is directly related to the surface energy of the solid material to be measured. Over the years, many methods have been developed to determine this important parameter. Dyne solution test may be the most commonly used monitoring technique by the converters in the related polymer film industries.

According to Young's equation [60], under standard conditions, a drop of liquid resting on the solid surface is balanced by the forces of γ_l , γ_s , and γ_{sl} as shown in Figure II-1.



$$\gamma_l \cdot \cos\theta = \gamma_s - \gamma_{sl} \quad (\text{Young's equation})$$

where γ_l is surface energy of gas-liquid interface

γ_s is surface energy of gas-solid interface

γ_{sl} is surface energy of solid-liquid interface, and

θ is contact angle.

Figure II-1 Force Balance of a Liquid Droplet on a flat Surface

The difference between the surface energy of gas-solid and liquid-solid interfaces is defined as the wetting tension of the solid surfaces. In the particular case of contact angle $\theta = 0$, the wetting tension of the solid will be the liquid surface energy. A series of liquid mixtures are specially designed with different surface energy values. When a particular liquid is spread on the polymer film surface, one of the three type behaviors of the liquid film occurs. The liquid film remains unbroken after two (2) seconds, which means that polymer film surface energy is higher than that of the liquid. The test needs to be repeated using another liquid with higher surface energy. The liquid film breaks within two (2) seconds, which means that polymer film surface energy is lower than that of the liquid. A lower surface energy liquid should be retried until the liquid film begins to break up into droplets at two seconds. In this case, the wetting tension of the polymer film is given by this particular liquid mixture. As defined in ASTM designation of D 2578-94 [61], the test liquid is the mixture of formamide and ethylene glycol monoethyl ether. It should be noticed that both of these solvents are classified as "light toxic" and require extensive safety precautions to use. In addition ethylene glycol monoethyl ether is highly flammable.

These dyne fluids are commercially available from several sources. A detail testing procedure is described in the document of D 2578-94 "Standard Testing Method for Wetting Tension of polyethylene and polypropylene films" [61]. This standard requires that the material be preconditioned at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity for at least 40 Hrs. But for plasma or corona treated polymer films, the test is usually done immediately after the treatment. During testing, minimum amount of solution should be

used since an excess can distort reading. The solution bottle should be capped to prevent solvent evaporation and contamination.

The contact angle is also widely employed to characterize the solid surface properties [62~63]. The smaller the contact angle is, the higher the solid-surface energy and better wettability it has. There is general agreement that a contact angle larger than 90 degree implies poor wettability. Instruments developed for contact angle measurement make it more accurate than dyne solution test.

The Dyne solution test and the contact angle test offer a practical and convenient method to evaluate the relative surface energy and the water affinity for smooth surfaces. In the case of fabrics as nonwoven web, the rough surface causes these methods to be less accurate. They also do not provide chemical component information of the surfaces.

4.2 Scanning Electron Microscopy

Electron microscopy, like light microscopy, includes scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM is frequently used to investigate the surface structure of the solid polymers. TEM can be used to test ultra-thin cross sections of fibers [47]. The main elements of a SEM apparatus are electron gun, electromagnetic lenses for focussing electrons, sample chamber with specimen stage and detectors and electronic system to display images. The magnification of a modern SEM ranges from 10X to 10,000X with resolution up to 0.01 μm . Usually the solid polymers are non-conductive. In order to prevent charging produced by the electron bombardment, the samples need to be coated with an

extremely thin conductive layer in high vacuum chamber. The coating conductive materials can be carbon or metals such as silver (Ag) and gold (Au) [64].

Ryosuke Koishi and coworkers [65] observed the topography of the thin film produced by carbon sputtering and plasma polymerization. They found the surface of sputtered carbon film consisted of larger clusters on the order of 10nm, while the plasma polymerized film had a much more smooth surface. Tsai, Wadswards and coworker [32] reported the entire surface changes of PP melt blown fibers after plasma treatment. They proposed that the change might be a result of chemical reactions and surface etchings. In the field of fiber enforced composites, the SEM technique is very helpful in investigating the fracture surfaces and analyzing the bonding modes. According to the research results from J. R. Brown and coworkers [39~41], scanning electron microscopy of shear fracture surfaces showed clean fiber/matrix separation in composites made from untreated fibers, indicative of weak interfacial bonding. In contrast, shear fracture surfaces of the composites containing plasma treated fibers exhibit clear evidence of fiber fibrillation and matrix cracking, suggesting strong interfacial bonding.

4.3 Electron Spectroscopy for Chemical Analysis (ESCA or XPS)

ESCA provides a convenient means to study chemical elements on polymer surface. It involves the measurement of energy and intensity of photoelectrons ejected from a surface following x-ray photoionization. Considerable work in this field had already been completed. An ESCA spectrum illustrates the information of binding energies and peak intensities. With appropriate calibration, the relative intensities and

shifts in binding energy for components can be used to identify structural features. By curve fitting and integrating, the peak areas can be achieved, which represent the particular element amount on the super-surfaces. For example, the overall O_{1s}/C_{1s} ratio shows the polymer surface components and compositions of oxygen and carbon. Therefore, the relevant surface phenomena such as weathering, oxidative degradation, surface modification, surface contamination and migration, can be investigated by ESCA for definite studies. In the field of plasma surface modification, ESCA is almost the essential tool of characterizing the plasma treatment effectiveness and it provides important information for surface and plasma chemistry researchers. Unfortunately, the determination of the relative amount of chemically similar functional groups is often difficult.

Jangmi Ryu and coworkers [45] made ESCA studies to characterize the surface of the corona-discharged and plasma treated wool fibers. The research results elucidated the intensity increase of oxygen element and the decrease of the carbon element, which suggested the oxygen atom on the treated wool surface might exist in the form of $-CO-$ and $-COO-$. The change in hydrophilic properties on the fiber surface plays an important role in improving the color depth of wool fabrics.

Surface functional groups containing oxygen atoms increase the surface tension of the solid polymer, therefore provide better wettability to water. The concentration of functional groups evidently affects wettability but not simply determine it. Kikuko Yoshimura and coworkers [54] reported the preparation of hydrophilic polymer derived by plasma polymerization from oxygen containing organic monomers. Their ESCA spectra of the polymers showed that the wettability was also dependent upon spatial

arrangement of oxygen atoms within the polymer molecules. The oxygen containing functional groups at the polymer surface may orient toward inside and a less wettable surface may be obtained.

According to F. Denes et. al. [66], under plasma conditions, SiCl_4 is fragmented into extremely reactive species of silylium (silicenium) ions, which opened new ways for modification of inert polymeric surfaces, such as PP, PTFE etc. The mechanism study showed that the predominant fragments were SiCl_3^+ cations with the accompany of SiCl_2^+ and SiCl^+ species. The authors utilized high resolution ESCA to investigate the surface chemical components. Analytical results indicated significant silicon and oxygen atom content regardless the nature of the substrates.

5.4 Infrared Spectroscopy

The attenuated total reflection infrared spectroscopy (ATR-IR) and the fourier transition infrared spectroscopy (FTIR) are the two other effective methods for solid surface chemical analysis. Except the surface composition, ATR-IR also provides some information on orientation and/or degree of crystallinity [67, 68]. This technique requires a very good contact between the sample and the spectrometer prism, which may be a source of difficulty of rough or inflexible films. Comparing with ESCA, which measures surface with an order of a few tens of Angstroms, ATR-IR has a range of about $1\mu\text{m}$ and measures a relatively thick surface layer [69]. Plasma polymerization usually produces a relatively thick film that may reach the range of $1\mu\text{m}$ and can be characterized by ATR-IR technique. Monomer with different polar groups, such as 2-hydroethyl acrylate, glycidyl methacrylate, acrylic acid and methyl acrylate had been

evaluated for plasma reduced grafting onto the polyethylene surface by ATR-IR. The ATR-IR spectra showed clear evidence that acrylic acid, glycidyl methacrylate and methyl acrylate had been successfully grafted [68]. Qiu and coworkers [53] modified the surface of polyurethane (Tecoflet) by plasma reduced grafting polymerization of poly(ethylene glycol) methacrylate. The surface was characterized by means of ATR-IR, ESCA and other techniques. ATR-IR spectra indicated qualitatively that PEG chains were successfully grafted on the surface of Tecoflex films. The broad band detected around 3470cm^{-1} demonstrates the presence of free hydroxyl groups.

Due to high speed computation provided by modern technology, FTIR is now almost completely displaced the use of conventional IR instrument. An FTIR spectrum can be obtained in a few seconds rather than a few minutes that allows many spectra to be accumulated and added together by the computer. Mounting sample is not a problem for FTIR. It measures all energy and none of lost, thus weak signals from strong absorbing samples can give good spectra. In combination with special techniques such as emission spectroscopy and photo-acoustic spectroscopy, FTIR can also analyze opaque samples without any difficulty [77].

5. Summary and Research Objectives

The functional groups introduced on to the hydrophobic fabric surface improve the surface energy and the affinity to the dye molecules. Since the color has immediate relationship with the amount of dye in the fiber and its distribution, a proper amount of dye must be adsorbed on the fiber surface and diffused into the bulk fiber; in other words, fiber should have suitable dye capacity. Research results on the dyeability of

plasma treated wool, cotton, PET and Nylon have been described [13,70~72]. Dye molecules can penetrate these fibers so they have relatively high dye capacity. With respect to PP and PE fiber, only the outmost surface, which is in the range of tens of nanometers, is capable of being plasma modified. It can pick up a very small amount of dye and may not diffuse into the inner parts of fiber. The small dye capacity results in only pale color. Extensive researches related to polymer surface modification have been published, but only few of them deal with the dyeability of PP and PE fibers. Furthermore, it seems that most attention has been paid to the introduction of functional groups, the dye capacity has been nearly ignored in the literature.

The objectives of this project include the following topics.

1. Investigating the effects of plasma treatment on the dyeability of PET and PP spunbond nonwoven webs,
2. Learning what happens on the fiber surface after plasma treatment by proper surface characterization tools.
3. Establishing a way to dye these hydrophobic fibers using water soluble dyes, which is more environmentally friendly.
4. Evaluating the effects of plasma treatment on the mechanical properties of PET and PP SB webs.

III. EXPERIMENTAL

1. Materials

Spunbond PET nonwoven webs, 50.3g/sq.m.,

Spunbond PP nonwoven web, 18g/sq. m.,

Compressed gases: SO₂, O₂ (99.8%), N₂ (99.998%), H₂ (99.99%), He (99.997%), Air,
(National Welder Supply Co.),

Acetic Acid, Glacial (Fisher Scientific Company),

Ammonium acetate, crystal (Fisher Scientific Company),

Triton X-100 (Rohm & Haas),

ORCO DYE CARRIER LO (Organic Dyestuffs Corporation),

Disperse blue (INTRASIL[®] Blue BGL-N, Crompton & Knowles Corporation),

Acid red (NYLANTHRENE[®] Red B-2BSA, Crompton & Knowles Corporation),

Acid blue (Acid Blue 284, Carolina Color & Chemical Company),

Detergent FL-70[®] (Fisher Scientific Company)

2 Plasma treatment

PET and PP spunbond nonwoven webs were continuously treated in a TANDEC high pressure plasma reactor designed to use at pressure ranging from 50 to 800 Torrs. The mixtures of (SO₂+O₂) and (N₂+He+H₂) were employed as working gases under system pressure of 696 Torrs. The power and treatment time were set differently according to the experiment design. PP SB nonwoven webs were also treated with an atmospheric plasma using air as working gas.

3. Wettability:

Wettability was qualitatively measured by observing the contact angle of a drop of distilled water on nonwoven web surface. Based on the standard of "AATCC Test Method 39-1974", it can also be evaluated by measuring the penetrating time required for a drop of distilled water to pass through the web. A smaller contact angle or shorter penetrating time illustrates a better wettability.

4. Dyeing processing:

The plasma treated samples and control were dyed in a TEXOMAT dyeing machine (AHIBA AG Lalorapparate, Chemie, Textile). A disperse dye, BGL-N (blue), and two acid dyes (Red B-2BSA, and acid blue 284) were employed. Samples including control were cut into different shapes with a total weight of 6.4 grams. They were wet-out in 0.1% Triton X-100 solution.

For the disperse dye, the dye bath was filled with 66 ml distilled water, 12 ml Triton X-100 solution (5%), 12 ml of carrier solution (50g/L). The temperature of the dye bath was raised to 110°F and then wet-out samples were added. 15 minutes later, total 40 ml of pre-dispersed dye solution (2g/L) was added and the temperature was raised to 212 °F. It was run 45 min and then the bath temperature was cooled down to 170 °F and run 30 min. The bath temperature was cooled further to 150°F and then the samples were removed and washed in running hot water. The whole procedure was repeated except that 12ml of carrier solution was replaced by 12 ml-distilled water.

For the acid dye, the wet-out samples were entered into the dye bath which contained 90ml distilled water, 50ml of acetic acid solution (10.8%) and 60ml of ammonium acetate solution (10%) at 110°F. After 15 minutes, 100ml of pre-dissolved acid dye (2g/L) was added and the temperature was raised to 210°F over a period of 45 minutes. It was cooled to 160°F and then the samples were removed and washed in soap. By changing the volume ratio of the buffer solution, the dye bath was set in different pH values.

5. Colorimetric Analysis:

The colored PET and PP nonwoven webs were folded into eight and sixteen layers, respectively. The color measurements were carried out with an colorimeter (Ocean Optics S1000) and the software of SPECTROSCOP™. Based on the CIE system (International Commission on Illumination), the instrument was properly calibrated using the supplier provided standard. The chromaticity coordinates L^* , a^* , b^* were obtained and the color differences ΔE^* were determined by using the following formula [64]:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

$$\text{With } \Delta L^* = L^*_{\text{sample}} - L^*_{\text{control}}$$

$$\Delta a^* = a^*_{\text{sample}} - a^*_{\text{control}}$$

$$\Delta b^* = b^*_{\text{sample}} - b^*_{\text{control}}$$

where L^* is brightness, a^* is yellow-blue and b^* is red-green. These parameters quantitatively describe the color and reflect the level of dyeing and color difference in the samples.

6. Differential scanning calorimetry (DSC):

DSC scan was carried out using a METTLER DSC 25 to measure the crystallinity of these samples. The starting temperature is 50°C and is programmatically raised at a rate of 10°C per minute. The scanning was determined at 300°C. The degree of crystallinity X_c can be calculated using the following equation:

$$\%X_c = \Delta H_s / \Delta H_\infty \times 100 \% [64]:$$

Where: ΔH_s is the melt enthalpy of sample

ΔH_∞ is the melt enthalpy of complete crystalline sample

7. Optical Microscopy (Cross-section Observation)

In order to make a good cross-section slide, fibers must be embedded in proper medium first. According to Spurr [73] , the following embedding medium formula was employed:

Spurr Embedding Medium

VCD (Epoxy resin)	2.5g
DER (Flexibilizer)	1.5g
NSA (Hardener)	6.5g
DMAE (Accelerator)	0.1g

where VCD is vinyl cyclohexene dioxide (ERL-4206), DER is 736 epoxy resin (diglycidyl ether of polypropylene glycol), NSA is nonenyl succinic anhydride, and DMAE is dimethylaminoethanol The fiber samples were mounded in the mixture of these

chemicals for a period of time. Under room temperature, approximately 24 hours were allowed for solidification.

Spurr embedding medium provided both proper affinity to PET and PP fibers and hardness for Microton slicing. A newly made glass knife was employed. Slices were microtonned into one and two microns, separately. After cutting, the plastic slides were transferred onto glass carriers. A drop of 10% acetone solution was added on to the slide to make the section flat, and then they were coated by 0.5% gelatin to keep them in position. The glass carriers were then put on slide warmer (60°C) to remove the solvents

An Olympus CH microscope and a software (IMAGE by NIMH) were employed to observe the cross-section and measure the diameter of fiber.

8. Scanning Electronic Microscopy (SEM):

The surfaces of plasma treated and untreated fibers were observed by SEM (ETEC Autoscan) and were recorded as photographs. The magnification of the image was set in the range of 1000X to 1500X.

9. Fourier Transition Infrared Spectroscopy (FTIR)

Plasma treated fibers were investigated by the technique of FTIR. All spectra were recorded by utilizing a Nicilet 20DVB FTIR spectrometer with an MTEC Model 100 PA cell. The reference material used was carbon black and the purging and conducting gas in the PA cell was helium. Each spectrum had 100 scans. There was no base line correction or smooth function used.

10. Tensile Properties:

Samples were stabilized under standard temperature/humidity condition for 24hrs before test. An United tensile tester was employed. Each sample was measured 10 times and the results were printed out directly by a connected computer. Limited by the original samples, tensile properties were measured only in machine direction.

IV. RESULTS AND DISCUSSION

1 Improved Dyeability of PET Spunbond Nonwoven Webs

1.1 Dyeability and Functional groups

The dyeability of spunbond (SB) PET nonwoven webs was significantly improved by ($\text{SO}_2 + \text{O}_2$) and ($\text{N}_2 + \text{H}_2 + \text{He}$) plasma, respectively. The data of color measurements were summarized in Table IV-1 and plotted in Figure IV-1 and IV-2. The chromaticity coordinates in Table IV-1 are widely used in industry to describe the color, color intensity, color difference and dyeing level of fibers. The parameter of L^* represents lightness, it is a number between zero (0) and a hundred (100). The coordinates of a^* and b^* are used to describe the color. A positive a^* means a reddish color and a negative a^* denotes a greenish color. Similarly, a sample with positive b^* is yellowish and negative b^* is bluish. The bigger the absolute values, the higher color intensity in its corresponding direction. The parameter of ΔE^* denotes the color difference between samples and control or selected standard. Because samples were colored red, all a^* s are positive. Comparing to control, plasma treated samples attained increased a^* value, which indicated the improved dyeability. PET samples treated by ($\text{SO}_2 + \text{O}_2$) plasma had much higher a^* value than that treated by ($\text{N}_2 + \text{H}_2 + \text{He}$) plasma. It was clearly showed in Table IV-1 that the color differences increase with the plasma treatment time. The lightness L^* displayed the reverse trends.

The color differences were also evaluated using the AATCC method of "Gray Scale for Color Change" [74] and were correlated to ΔE^* measured by colorimeter. It was found that a value of ΔE^* being equal to or bigger than 1.8 could be regarded as

Table IV-1. Color Measurement of PET Samples Dyed by Acid Red

Sample	Plasma conditions		L*	a*	b*	ΔE^*	Gray Scale ¹
0110PET-III-1	3* SO ₂ + 0.1* O ₂ P=400/75 (325W) T=102°F, p=696 Torr	10 sec	66.862	20.486	2.390	21.029	1~2
0110PET-III-2		15 sec	40.164	46.461	41.119	71.832	1
0110PET-III-3	10*N ₂ +1.5*He +0.25*H ₂ P=350/50 (300W) T=85°F, p=696 Torr	30 sec	74.388	4.810	-2.028	4.402	2
0110PET-III-4		15 sec	76.806	3.741	-1.564	1.817	2~3
0110PET-III-5		10 sec	78.470	3.726	-1.937	0.271	4
Control	----	---	78.597	3.542	-1.785	---	---

Note: 1, much change; 2, considerably change; 3, noticeable change; 4, slightly change; 5, no change. [74]

significant difference. The great difference of dyeability before and after plasma treatment strongly indicated that plasma caused a big change to SB PET fiber, which could be in both chemical and physical properties.

Plasma creates many reactive species such as free radicals. They may start a variety of reactions, for example, grafting reactions, polymerization and chain scissions, even the reactions that may not occur in the frame of traditional organic chemistry. The data in Table IV-1 suggested that the polar functional groups were introduced onto the fiber surface (and more evidence was given in Chapter IV, Section 3.3). The types of functional groups are partially determined by the working gas. It is accepted that amino

other nitrogen containing functional groups were implanted onto the PET fiber surfaces because working gas (N_2+H_2+He) was employed. It is also suggested that the density of the functional groups increased with the plasma treatment time in a proper extent. Higher functional group density provides more active sites on the fiber surface and higher possibility for improving dye take-up. Therefore it created increased color difference as plasma treatment time was prolonged, as illustrated in Figure IV-1.

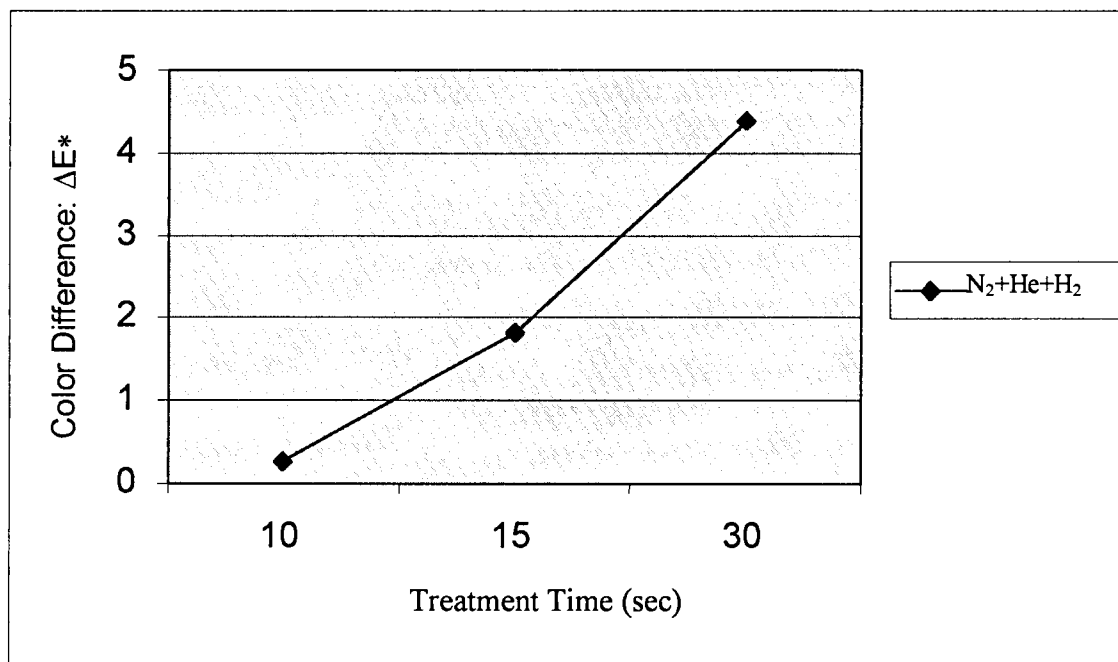


Figure IV-1. Color difference as a function of plasma treatment time with working gas: ($N_2 + H_2 + He$) and acid dye

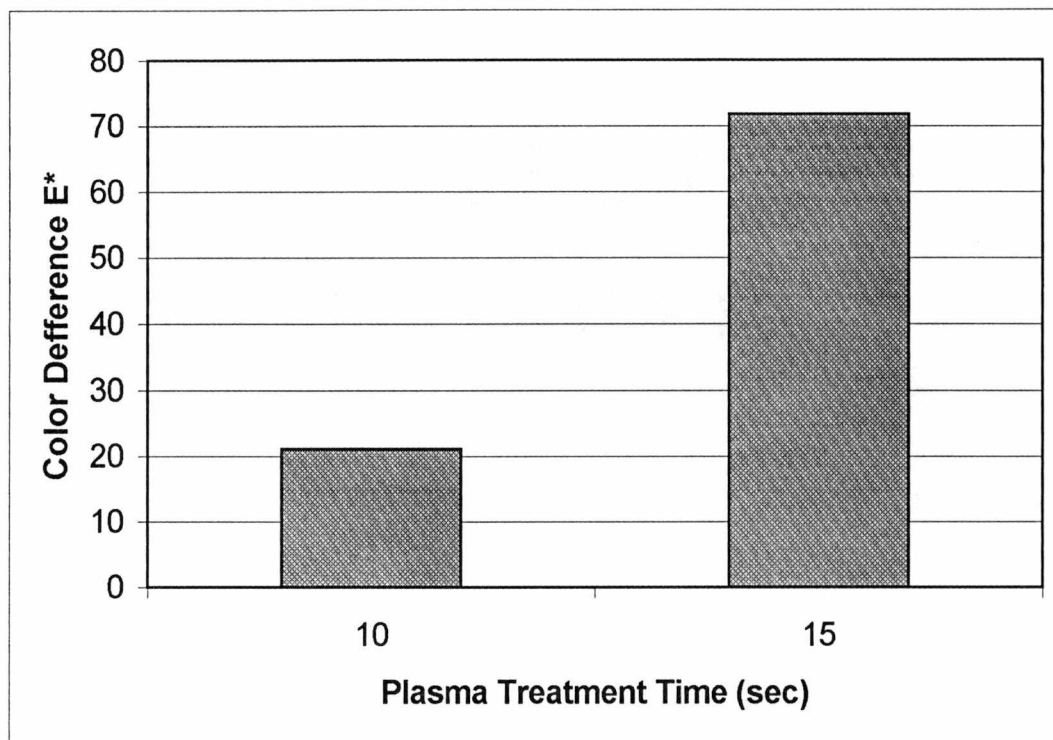


Figure IV-2. Color difference as a function of plasma treatment time with working gas (SO_2+O_2) and acid dye

According to Figure IV-2, the (SO_2+O_2) plasma seems to be much more effective than the ($\text{N}_2+\text{H}_2+\text{He}$) plasma. The (SO_2+O_2) plasma gave rise to much higher color difference. The samples treated by (SO_2+O_2) plasma showed bright and deep color. This phenomenon may be controlled by the chemical natures of the working gas (SO_2+O_2) and hinted more polar groups on fiber surface. Oxygen is very reactive and oxygen free radicals are 10^4 times more active than oxygen molecules [80]. The free radicals of sulfur dioxide are also strong oxidative and highly reactive. The sulfur and oxygen elements have higher atomic mass so that the active species from SO_2 and O_2 have higher molecular weights than that of N_2 , which may result in higher kinetic energy, although under relative high pressure this factor may not be so important. These factors allow

(SO₂+O₂) plasma more efficient in introducing functional groups to fiber surfaces. These polar groups are believed oxygen containing or sulfur-and-oxygen containing and strongly hydrophilic. The functional layer on fiber surface possesses the affinity for water and water soluble dyes, which improves the dye take-up, i.e., improves the dyeability.

The samples treated by (N₂+H₂+He) plasma also showed good shade. These data suggested that after proper plasma treatment, PET SB nonwoven web could be colored by traditional water-soluble acid dyes.

1.2 Dyeability and Crystallinity

By limiting the influences of functional groups, the other effects of plasma treatment on dyeability might be found. Based on this idea, the (N₂+H₂+He) plasma treated PET SB nonwoven webs were colored by a disperse dye (BGL-N blue) using conventional dyeing processing. For they are basically water insoluble, disperse dyeing are more affected by the fiber structure. Disperse dye penetrates into the dyeable noncrystalline region mainly by diffusion. The dye molecules are fixed in fibers by the means of disperse forces. The color measurements were shown in Table IV-2 and plotted in Figure IV-3.

These data suggested that plasma treatment reduced the dyeability for disperse dye, which are apparently conflict with that we reached above. A hydrophilic fiber surface is definitely benefit to disperse dyeing because the swelled surface during dyeing provides more space for disperse dye molecules to penetrate inside. But it seemed not very important. To understand these results, enthalpy measurements by DSC technique

Table IV-2. Color measurement of PET samples dyed by disperse blue

Sample	Plasma Conditions		L*	a*	b*	ΔE^*
0110PET-III-3	10*N ₂ +1.5*He +0.25*H ₂ P=350/50 (300W) T=85°F, p=696 Torr	30sec	25.940	17.830	-53.39	3.705
0110PET-III-4		15sec	24.119	19.385	-53.24	4.079
0110PET-III-5		10sec	22.294	20.993	-54.35	6.402
Control			24.846	17.134	-49.92	

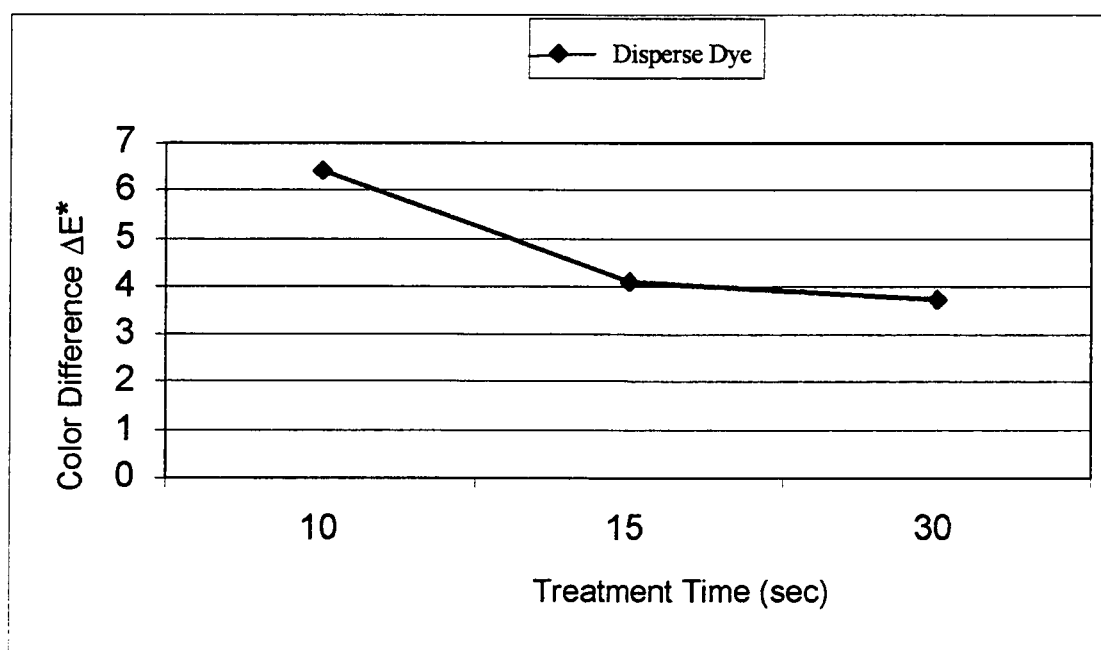


Figure IV-3. Color Difference as A Function of Plasma Treatment Time with Working Gas (N₂ + H₂ + He) and Disperse Dye

were performed. The data summarized in Table IV-3 were illustrated in Figure IV-4. It was showed that crystallinity was increased slightly as the treatment time increased. It is well know that the crystallinity of conventional textile PET fiber is around 40~50%. Comparatively, PET fiber produced in spunbond nonwoven processing has quite low crystallinity (Table IV-3). This is mainly because of the low crystallization speed and low draw ratio during the fiber production.

The plasma consists of chemically active and kinetically energetic species, which interacts with the polymer surface macromolecules. The energetic species collide with the polymer surface and transfer energy to the molecules, which may raise the temperature of

Table IV-3. Melt Enthalpy and Crystallinity Measured by DSC Analysis

Samples	Working gas	Treatment time (sec)	ΔH_s (J/g)	Crystallinity (%)
0110PET-III-1	(SO ₂ + O ₂)	10	50.2	35.86
0110PET-III-2		15	51.8	37.00
0110PET-III-3	(N ₂ +H ₂ +He)	30	43.3	30.93
0110PET-III-4		15	37.9	27.07
0110PET-III-5		10	37.1	26.50
CONTROL	-----	-----	33.1	23.64

Note: $\Delta H_\infty = 140$ J/g [81]

the surface. Under proper plasma conditions, the temperature falls in the range that is suitable for crystallization. A longer treatment time provided more opportunity for heat transfer and crystalline development. It would be reasonable that the inner of the fiber was less affected by plasma treatment.

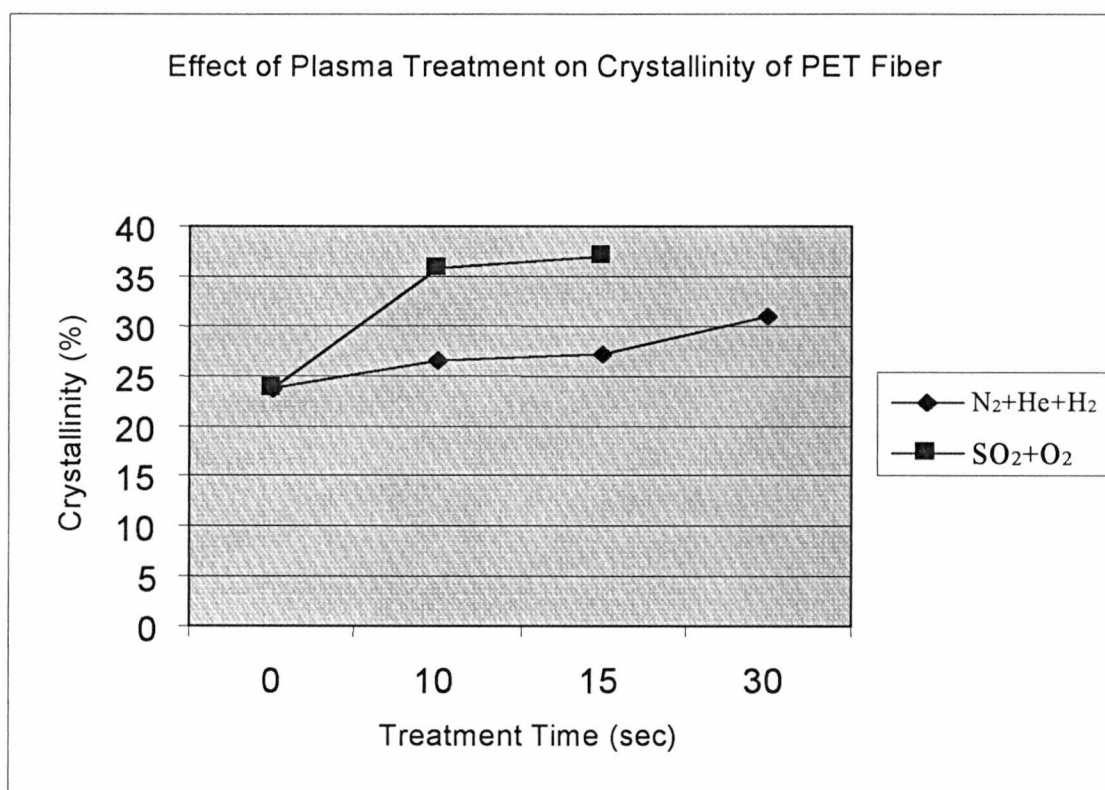


Figure IV-4. Effect of Plasma Treatment on Crystallinity of PET Fibers

The other possible reason might be related to the drawing force. Because these PET SB nonwoven webs were plasma treated continuously, the force loaded on the web along machine direction (MD) likely helped the crystallinity increase. This phenomenon could also be explained by another published theory. According to T. Okuno and co-workers [82], the plasma species preferentially interact with the macromolecules in the amorphous phase and partly etch them away, by which the crystallinity is relatively increased.

According to the dyeing principles, crystalline region does not allow the dye molecule to penetrate, i.e., increased crystallinity reduces the dyeability. This theory is provided more evidence by the present research results. With the treatment time increasing, surface crystallinity was increased and the dyeable noncrystalline region was reduced simultaneously, which resulted in the decrease of disperse dye take-up and thus lowered color differences. Former research pointed out cross-linking occurred among the surface macromolecules during plasma exercising. Consequently, it may also retard the coloration of the PET webs.

In the case of acid dye, the plasma treatment improved the dyeability significantly, even though the increased crystallinity reduces dye take-up in some degree. It actually proven that the functional groups play a predominant role in improving the dyeability.

1.3 Dyeing Conditions

By conventional dyeing processing, we have already found that plasma treatment significantly increased the dyeability of PET SB web for water-soluble acid dyes. This is a very promising progress. It predicted an energy-saving and more environmentally friendly dyeing process. The next research target is to learn how the plasma treated PET SB webs behave under different dyeing conditions.

1.3.1 Experiment design

Three important variables were considered with different levels as shown in Table IV-4. Based on this table, three experiments at different dyeing temperatures were organized using TEXOMAT dyeing machine (AHIBA AG Laborapparate. Chemie Textile). Each experiment included three dyeing beakers with three (3) different pH dyeing solutions. Each beaker contained three (3) fabrics:

PET-1 ((SO₂ + O₂) plasma treated, 10 sec);

PET-2 ((SO₂ + O₂) plasma treated, 15 sec);

PET-0 (Without plasma treatment).

Each fabric had four pieces and was properly loaded on the sample frame so that these pieces could be taken out of the beaker at a proper time. All of these samples (3×3×3×4) were properly washed in soap. After dried in air, they were ironed with a steam iron.

Table IV-4 Experiment Design for Dyeing of (SO₂ + O₂) Plasma Treated
PET Spunbond Webs

LEVELS	VARIABLES		
	Dyeing Temp (°F)	Dyeing Time (min)	pH
1	172	15	4.77
2	192	30	4.95
3	212	45	5.12
4	----	60	----

1.3.2 Dyeing temperature

PET SB nonwoven webs were dyed using an acid blue (C.I. Acid blue 284). Dyeing temperature is a very important factor in dyeing procedure. As shown in Table IV-5 and Figure IV-5, the color difference ΔE_0^* of control increased with the dyeing temperature. However, the color difference ΔE^* of plasma treated PET samples indicated a decreasing trend as the dyeing temperature increased (Figure IV-6)

Table IV-5: Color Measurement of Plasma Treated PET-1 SB Web Under Different Dyeing Temperatures.

Sample ID	Temp. (°F)	pH	Time (min)	L*	A*	b*	ΔE*	ΔE ₀ * ¹
08021-1	172	4.77	30	12.50	15.38	-22.92	49.08	82.34
PET-0				60.60	9.30	-15.98		34.87
09021-1	192	4.77	30	13.32	17.27	-24.17	45.93	82.31
PET-0				58.52	24.27	-19.89		44.56
10021-1	212	4.77	30	25.44	22.38	-25.51	30.01	73.03
PET-0				54.42	27.92	-20.01		49.52
08031-1	172	4.77	45	13.11	15.82	-23.61	49.08	82.05
PET-0				61.40	11.24	-16.14		34.92
09031-1	192	4.77	45	16.12	18.38	-24.41	36.44	80.03
PET-0				51.11	28.06	-21.35		52.57
10031-1	212	4.77	45	16.37	20.96	-25.62	38.39	80.81
PET-0				52.60	31.92	-19.22		52.80
08041-1	172	4.77	60	4.52	28.74	-6.44	55.41	90.24
PET-0				57.23	15.68	-17.45		40.45
09041-1	192	4.77	60	5.87	29.87	-5.99	47.00	89.30
PET-0				50.63	28.39	-20.25		52.64
10041-1	212	4.77	60	12.94	20.91	-23.11	38.40	83.17
PET-0				49.59	31.56	-18.94		54.66
Undyed white PET SB Web ¹				89.88	0.4	0.9		

Note: The color difference was calculated using an undyed white PET SB web as standard.

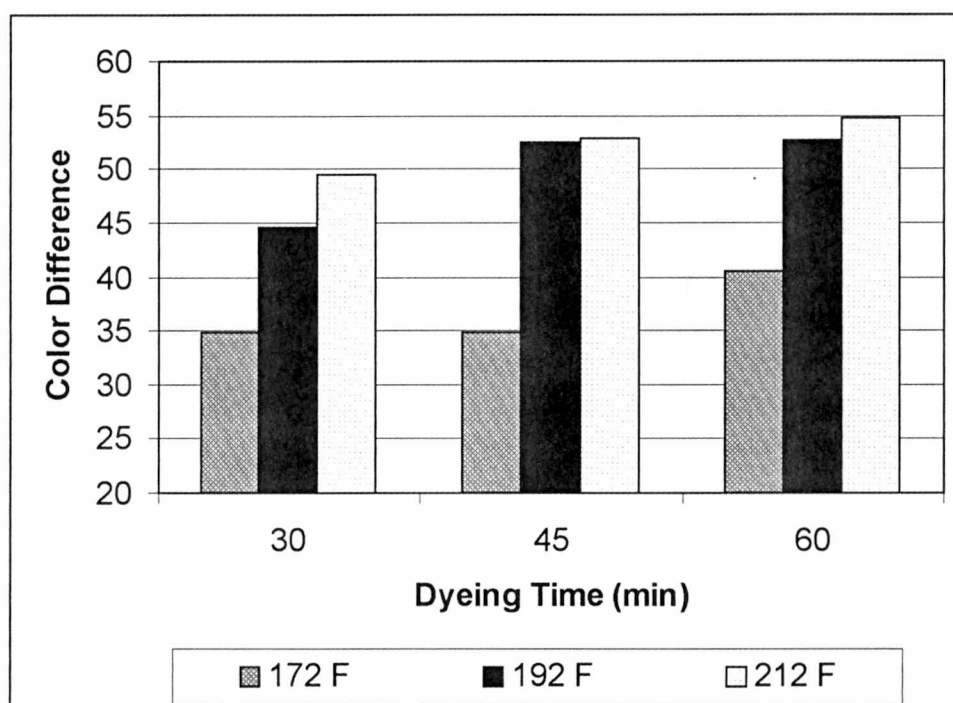
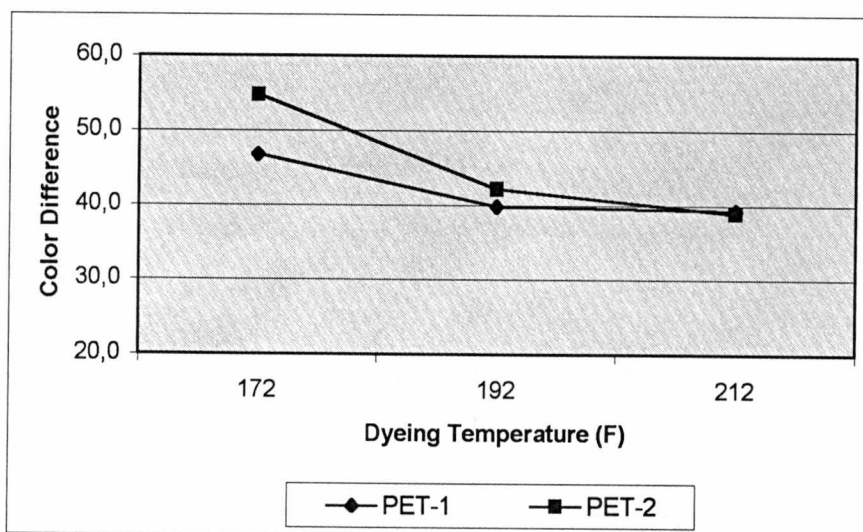
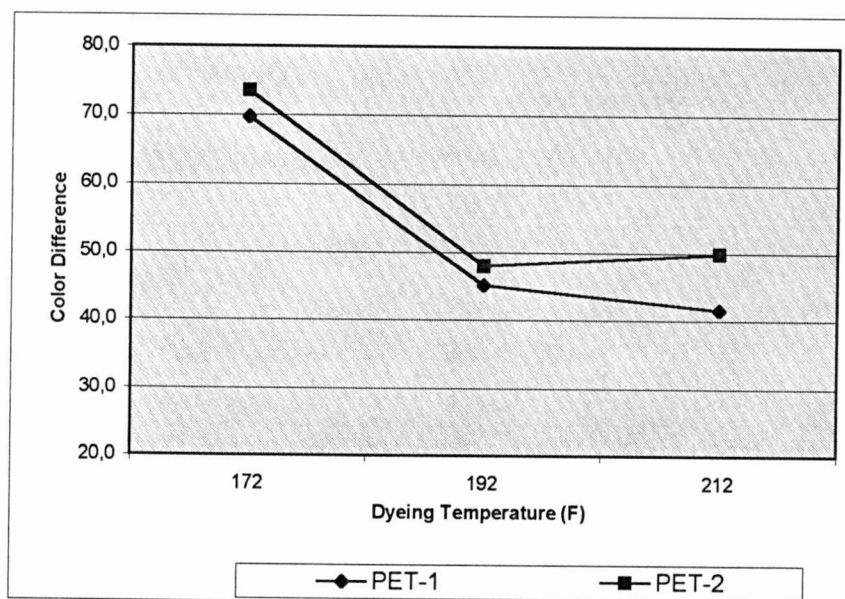


Figure IV-5 Effect of Dyeing Temperature on Color Difference ΔE_0^* of Controls



(a)



(b)

Figure IV-6 Effect of Dyeing Temperature on Color Difference ΔE^*

(a): 60 min, pH=4.95 (b): 30min, pH=5.12

At low temperature, i.e., 172°F, which is lower than the glass transition temperature of PET ($T_g=185^\circ\text{F}$), PET molecular chains are not affected significantly and have difficulties to make movements. The relatively strong interaction among macromolecular chains prevented the dye molecules from penetrating into the fiber. This is the reason that control samples were only slightly colored. However plasma treated PET fibers had functional groups on the surface which provided the greatly improved affinity to the dye. The polarity of the functional groups allowed the fiber surface layer to attract dye molecules with much faster rate. The rate is comparatively slow for dye molecules to diffuse into untreated PET fiber. At this low temperature, the polar layer is the key, which contributed greatly to the higher color difference.

As the dyeing temperature raised up to 192°F (over T_g of PET), PET molecular chains in non-crystalline regions partially overcame the intermolecular forces and started segmental movements, which allowed dye molecules to diffuse in with less difficulties. Comparing at low temperature condition, diffusion is increasingly improved at the temperature over T_g of PET. On the other hand, the surface polar layer, which is limited by its capacity, is relatively easy to reach the dynamic equilibrium of dyeing. It was believed that (SO_2+O_2) plasma introduced oxygen-containing and oxygen-sulfur-containing functional groups and acidic groups. Acid dye molecules diffused in and interacted with these groups by H-bonds and van der Waals' forces. As the temperature increases, the adsorbed dye molecules could achieve high enough energy to overcome the interaction with the functional groups and partially return to the aqueous solution. That is why the color difference decreased as the temperature increased.

interaction with the functional groups and partially return to the aqueous solution. That is why the color difference decreased as the temperature increased.

These results evidently suggested the plasma treated PET SB fiber had a “Skin-Core” structure. The “skin” was the plasma functionalized polar layer, which preferred a relatively low temperature, and the “core” was the untreated inner part, which needs a higher temperature to promote the diffusion of dye molecules.

The sample of PET-1 and PET-2 were treated under same plasma conditions except treatment time, which is 10 sec and 15 sec, respectively. Figure IV-6 illustrated larger color difference for PET-2. It suggested that a properly longer plasma treatment time provided better effect or introduced more functional groups onto the fiber surface.

1.3.3 Dyeing Time

As the other dyeing conditions were set, it allowed the comparison of color difference (ΔE^*) while the dyeing time changed from 15 minutes to 60 minutes. The data were presented in Figure IV-7. This three dimensional (3-D) figure illustrated the relationship between color difference and dyeing time (t) as well as dyeing temperature (T). Because an undyed white PET SB web was used as standard, color difference ΔE_0^* was attained and was expected to closely reflect the shade of dyed samples to human eye.

It showed that color difference increased with dyeing time at different temperatures. It was logical because a longer time allows more dye molecules adsorbed on fiber surface and then eventually diffuse into the fiber. It also apparently suggested that ($\text{SO}_2 + \text{O}_2$) plasma treated PET SB web would be more properly dyed under a lower temperature (such as 192 F and 172F) for a longer time.

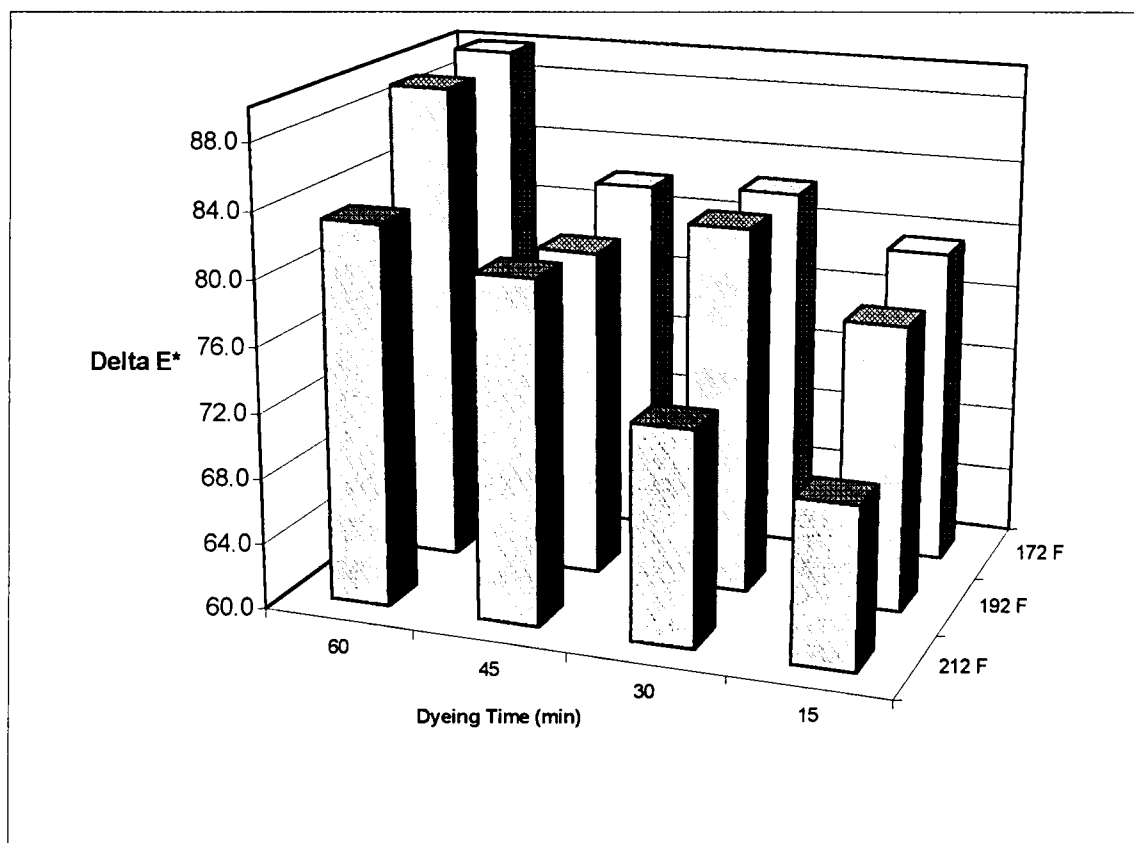


Figure IV-7 Effects of Dyeing Time and Dyeing Temperature on the Color Difference ΔE_0^* of Plasma Treated PET SB Fiber

All the dyeing behaviors were associated with the "Skin-Core" structure and the interactions between dye molecules, functionalized outer layer and inner PET macromolecular chains. It was expected that functional groups in the skin layer were oxygen-containing or sulfur-oxygen-containing and some of them were acidic. The example functionalities could be given as follows,

Carboxyl: —COOH ,

Carbonyl: —COH , —COR ,

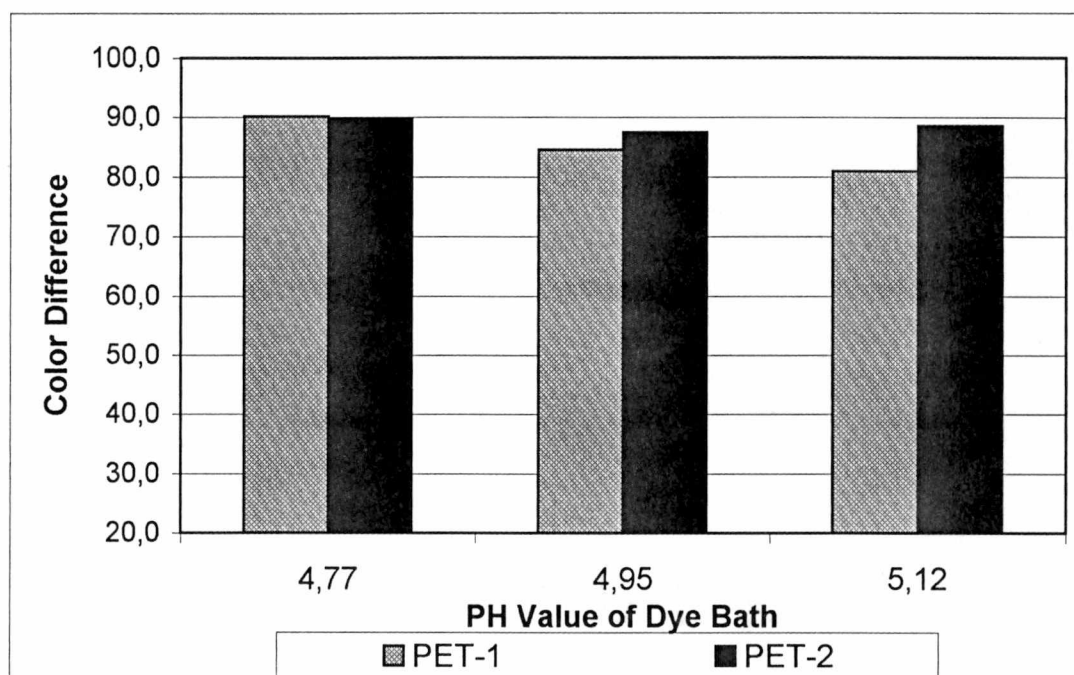
Hydroxyl: —OH ,

Sulfo: $\text{—OSO}_2\text{H}$.

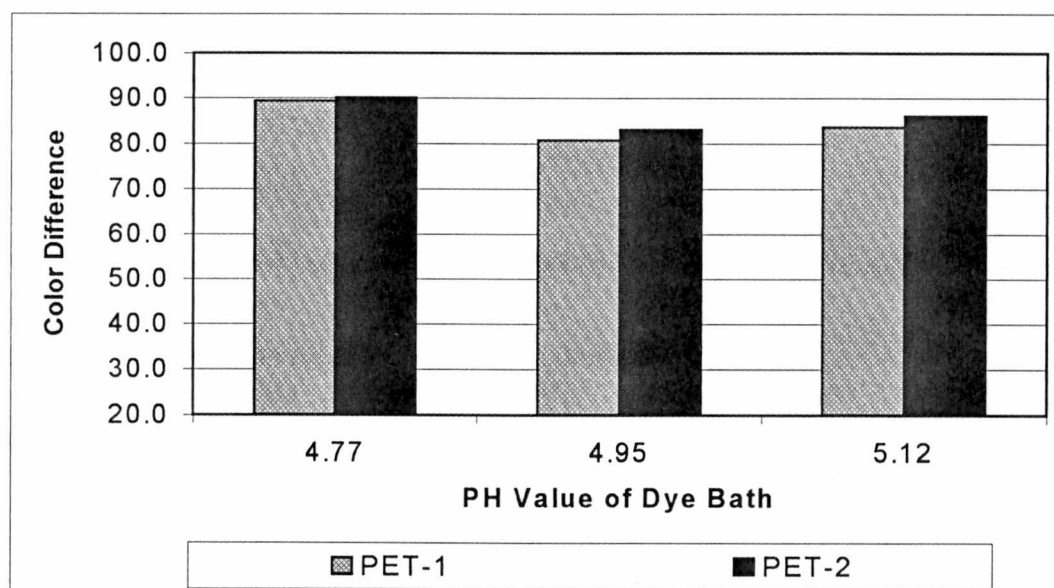
The hydrophilic property provided the affinity of plasma treated PET fiber to both water and dye molecules. Under the dyeing conditions, the swelled skin layer offers room for diffusion of dye molecules. Accordingly, there would no chemical reactions happened between these groups and acid dye molecules, but among them exist H-bonds and van der Waales' forces, which enabled dye molecules (carrying more than one amine and sulfate groups) well fixed in the fiber.

1.3.4 The pH value of dye bath

The pH value of dye bath is another critical factor of dyeing processing. It may change the color and activity of the dye, fiber surface property, rate of dyeing and the quality of dyeing. An acidic dyeing solution is essential for acid dyes. In this work, three levels of pH value were applied. As shown in Figure IV-8, pH value in the range applied did not make significant variation in color difference, even though a pH value at 4.77 was a little more desirable.

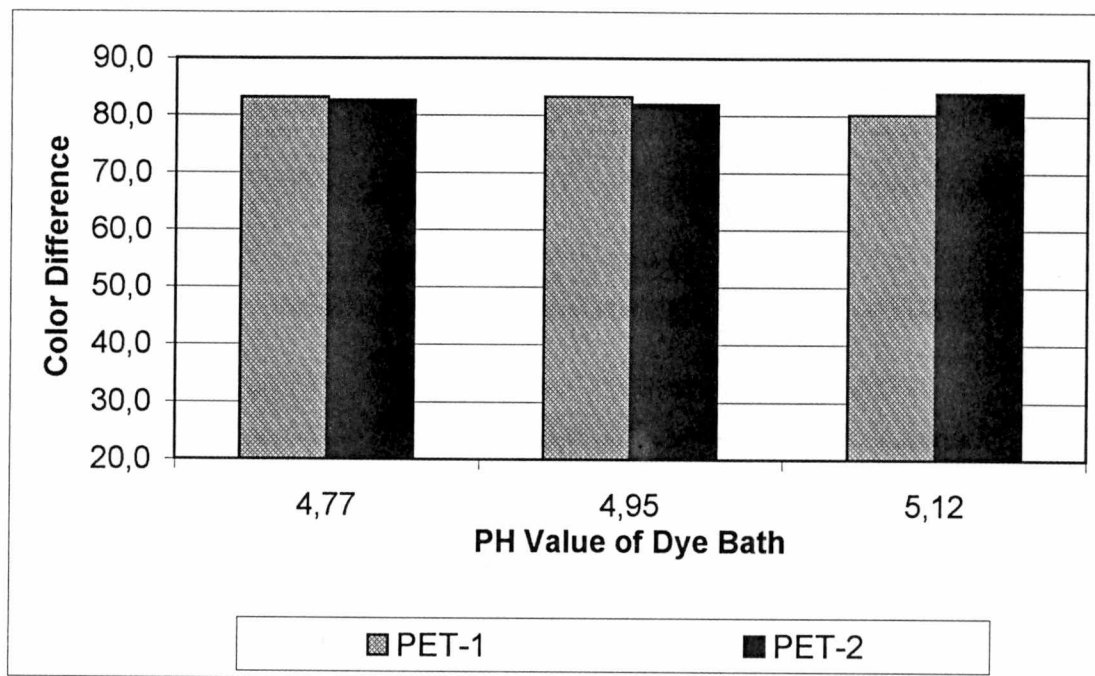


(a)



(b)

Figure IV-8 Effect of pH Value of Dye Bath on Color Difference
(a) 172°F, 60min; (b) 192°F, 60min; (c) 212°F, 60min



(c)

Figure IV-8 (continued)

1.3.5 Aging Of Plasma Treated PET SB Nonwoven Webs

It was reported that [79] that plasma treated PP film would partially lose its achieved properties, such as increased surface energy, especially during the first few days while exposed to air. This phenomenon was defined as “aging” of plasma treatment effect. The data in this research were shown in Table IV-6.

Based on these data, aging phenomenon was insignificant for (SO_2+O_2) plasma treated PET nonwoven web. These data supported the idea that functional groups were introduced on the fiber surface and suggested these groups were stable. This would be important in an industrial point of view because it would allow plasma treated PET SB fabrics transported to other places and even store for a period of time.

Table IV-6 Aging Of Plasma Treated PET SB Nonwoven Web

Samples	Newly Treated		Four (4) Months		Eight (8) Months		Twelve(12) Months	
	Wetting Time ¹	ΔE^*	Wetting Time	ΔE^*	Wetting Time	ΔE^*	Wetting Time	ΔE^*
PET-1	3~5 sec	45.65	8~12 sec	42.12	10~20 sec	41.35	10~20 sec	40.37
PET-2	1~3 sec	55.83	8~12 sec	52.89	10~20 sec	52.21	10~20 sec	48.58

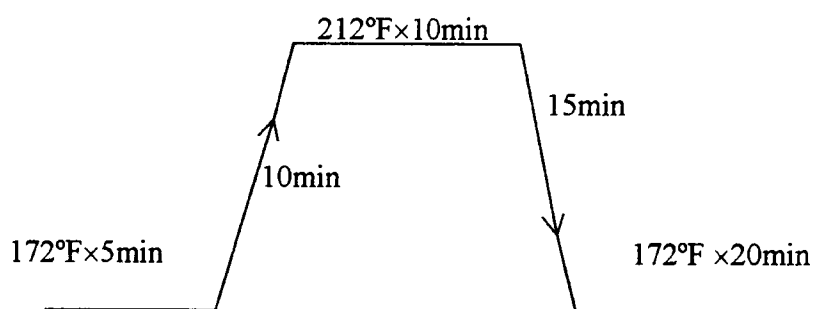
Note: 1. Samples were dyed using acid blue dye under 212°F for 60min. (pH=4.95)
 2. Wetting time was used in this work for defining the wettability.

1.3.6 Summary

It has been demonstrated (SO_2+O_2) plasma exhibited higher effectiveness than ($\text{N}_2+\text{H}_2+\text{He}$) plasma. PET SB webs treated with (SO_2+O_2) plasma can be readily colored by conventional acid dyes and showed commercially interested colors, which predicts the elimination of toxic carriers and easy control of discharged waste-water. This exciting progress may open a new way for coloring PET fiber or fabrics, which could be a revolution for dyeing hydrophobic plastic materials. The most important benefits include environmental friendliness and energy saving.

The research results concluded that the (SO_2+O_2) plasma treated PET SB fiber had a "Skin-Core" structure. The functionalized "Skin" layer plays the most important

role in the improved dyeing properties. It is pretty stable and allows transportation and storage of treated fabrics for a period of time. The pH value of 4.77, dyeing temperature of 172°F and dyeing time of 60 min are the favorite dyeing conditions. Considering higher temperature (212°F) have the function to promote dye molecule diffusing inside faster and the preferred temperature is 172°F, the author suggested an adjusted dyeing condition, which is showed as follows,



2. Improved Dyeability of PP Spunbond Nonwoven Webs

PP spunbond nonwoven webs were treated using (N_2+He+H_2) plasma. The plasma treated samples were colored by an acid blue and a disperse blue, respectively. The data of color measurement were shown in Table IV-7 and IV-8.

The color difference showed that the (N_2+He+H_2) plasma significantly increased the dyeability of PP spunbond nonwoven webs for acid dye. The treatment time affected the color difference with a manner illustrated in Figure IV-9.

Table IV-7. Color Measurement of PP Samples Dyed by Acid-Blue

Samples	Plasma Conditions		L*	a*	b*	ΔE^*
0110PP-II-1	10*N ₂ +1.5*He +0.25* H ₂ P=400/25 (375W) T=91°F, p=696 Torr	30sec	44.78	-17.68	-6.46	38.92
0110PP-II-3		15sec	45.06	-16.94	-5.53	38.31
0110PP-II-2		10sec	35.86	-24.63	-5.54	50.21
0110PP I	10*N ₂ + 0.25* H ₂ P=500/25 (475W) T = 68°F; p = 696 Torr	30 sec	37.58	-21.27	-6.54	46.63
0109PP	10*N ₂ +2*He+4* H ₂ P=500/50 (450W) T = 72°F; p = 696 Torr	5 sec	48.52	-8.27	-15.94	24.87
Control	-----	----	72.62	9.31	-9.86	----

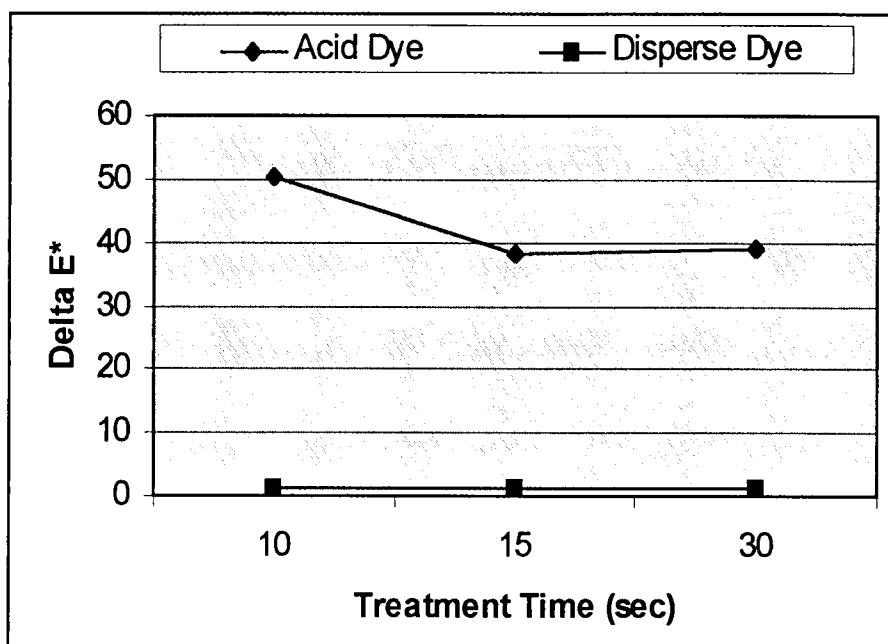


Figure IV-9 The Relationship Between Color Difference and Plasma Treatment Time [PP Web, The Plasma operating conditions were as follows, working gas $= (10 \cdot \text{N}_2 + 0.25 \cdot \text{H}_2 + 1.5 \cdot \text{He})$, Power=400/25 (375w), Temperature =91°F and pressure = 696 Torr]

Under the given plasma conditions, a time of ten seconds was long enough for good dyeability. With the increasing of treatment time, the dyeability was decreased and then kept in a relatively instant level, which seemed to suggest an equilibrium between implanting and removing functional groups during plasma treatment.

Functional groups implanted on the PP fiber surfaces were expected to be nitrogen containing, which provide active sites for acid dyes, whose molecules are fixed on the fiber surfaces by chemical bonds. On the other hand, for the nature of few reactive functional groups, disperse dye molecules can not fixed through chemical bonds. Its high crystallinity and total hydrophobic property of PP fiber prevents these disperse dye molecules from penetrating inside [Table IV-8]. These are the reasons that disperse dye did not work well for the plasma treated PP webs. It was proved again that functional

groups introduced by plasma treatment played the predominant role in the improved dyeability.

As observed, the nitrogen-containing functional groups introduced by (N_2+He+H_2) plasma treatment also provided PP webs with excellent wettability and extended to a period of several months. The data in Table IV-7 and IV-8 demonstrated that the improved dyeability of PP web is almost solely the function of surface functional groups and their density. Due to the functional groups can be implanted only on the fiber surface by plasma and dye molecules can hardly penetrate into fiber, high functional group density is required for sufficient dye-sites in order to provide commercially interesting color. Comparing PET, modifying PP by plasma treatment is a big challenge to both polymer scientists and plasma engineers.

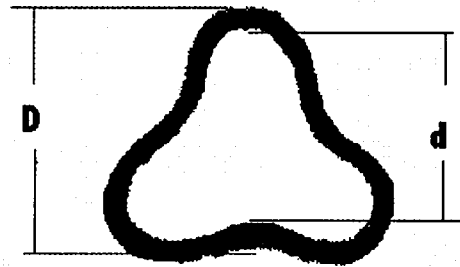
Table IV-8. Color Measurement of (N_2+He+H_2) Plasma treated PP Samples Dyed by Disperse-Blue

Samples	Plasma Conditions		L*	a*	b*	ΔE^*
0110PP -II-1	10*N ₂ +1.5*He +0.25* H ₂ P=400/25 (375W) T=91°F, p=696 Torr	30sec	80.51	-1.77	-0.15	1.09
0110PP -II-2		10sec	80.22	-1.63	-0.11	1.31
0110PP -II-3		15sec	81.08	-1.92	-0.21	1.16
0110PP -I	10*N ₂ + 0.25* H ₂ P=500/25 (475W) T = 68°F; p = 696 Torr	30 sec	80.50	-2.76	-1.46	1.44
Control	----	----	81.26	-1.67	-0.91	----

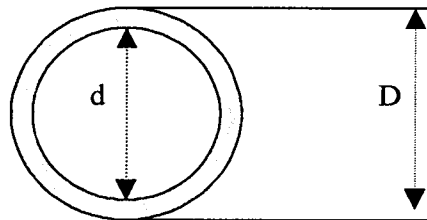
3. Surface Characterization of Plasma Treated PET & PP SB Fiber

3.1 Optical Microscopy

The purpose of this experiment is to observe the distribution of dye in the fiber. It also helps to understand the mechanism of plasma treatment. With the regular white light illumination, it was observed that the spunbond PP and PET fiber used in this work had different cross-sections, i.e., usual circular shape is for PP fiber and triangular or Mercedes shape for PET fiber, as shown in Figure IV-10 :



PET fiber



PP fiber

Figure IV-10 Cross-sections of PET Fiber and PP Fiber

The fiber diameter **D** was measured and the data were presented in Table IV-9. A drop of immersion oil ($n_{d, \text{oil}} = 1.515$ at 23°C) was put on the sample slide ($n_{d, \text{PET}} = 1.53\sim 1.54$ at 23°C [75]) for two hours at room temperature to allow the oil penetrate into the embedding medium and reach the fiber surface. The cross-sections of undyed fibers were almost invisible because the refractive indexes of PET and immersion oil are pretty close which extensively eliminates the affect of light reflection and refraction on the interface. However, for the plasma treated and colored fiber, the dark edge of its cross-section is still visible, which is due to the light adsorption by the dye molecules that distributed in this area.

The observation evidently showed that only the surface of the fiber was colored and no color was observed in the inner part of the fiber. This result provided further evidence that plasma treatment was a surface modification technology and also plasma treated fiber has a “Skin-Core” structure.

As shown in Figure IV-10, the distance **d** was also measured and the thickness of colored layer on fiber surface was calculated using the following formula:

$$T=(D-d)/2$$

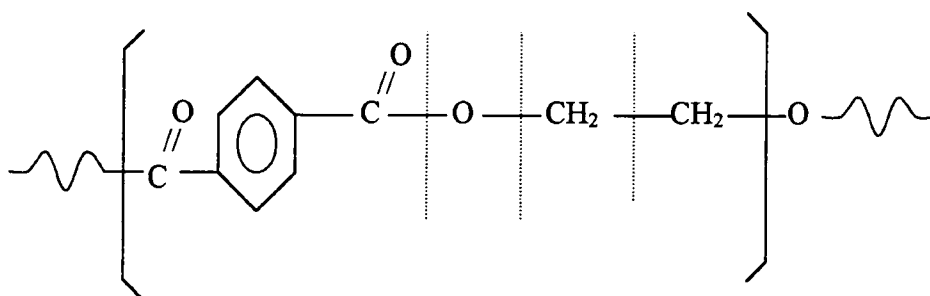
From the data presented in Table IV-9, it was showed that the thickness of plasma treatment is smaller than two (2) micron and a ($\text{SO}_2 + \text{O}_2$) plasma resulted in a larger treatment thickness than a ($\text{N}_2 + \text{He} + \text{H}_2$) plasma did. The reason for this result is that plasma treated PP only accepts dye on the modified surface, whereas plasma treated PET even allows dye molecules to diffuse further inside.

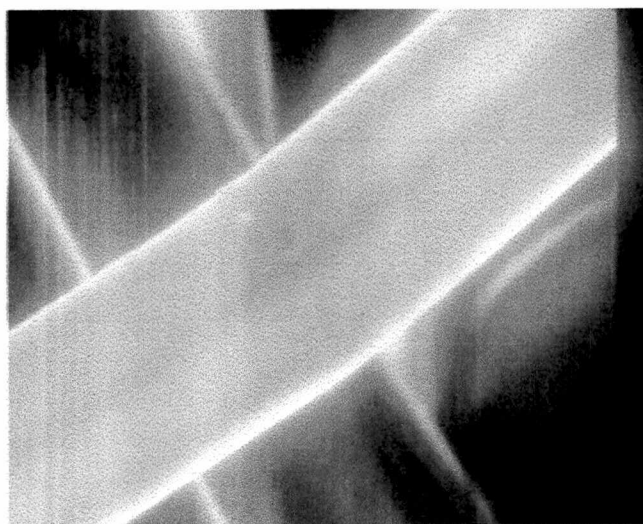
Table IV-9 Fiber Diameter and the Thickness of the “Skin” Layer Created by Plasma Treatment

Measures	PET-1		PET-2		PP	
	D (μm)	d (μm)	D (μm)	d (μm)	D (μm)	d (μm)
1	21.65	19.33	23.50	17.18	18.81	11.30
2	21.32	18.39	24.30	19.73	15.83	10.85
3	21.02	18.51	21.18	18.47	18.16	14.83
4	21.36	18.51	22.29	17.59	16.27	13.01
5	21.36	18.98	21.62	18.78	15.98	14.23
6	22.41	21.09	23.76	19.09	16.42	15.71
7	23.94	17.66	23.72	18.95	17.18	12.75
8	21.83	18.65	22.39	18.09	14.38	12.34
9	21.48	16.47	20.37	19.34	15.82	13.58
10	22.85	18.47	22.10	19.18	18.39	11.92
11	24.30	17.95	22.26	18.22	15.63	13.39
12	23.25	18.94	23.16	21.24	15.70	11.52
13	19.97	17.74	20.79	17.28	15.67	13.75
14	23.05	19.28	21.59	17.74	14.92	12.39
15	22.37	19.22	21.82	17.52	13.61	13.79
Average	22.14	18.61	22.32	18.56	16.18	13.02
STDV	1.1712	1.0177	1.1596	1.0898	1.4468	1.3526
Thickness	1.77		1.89		1.58	

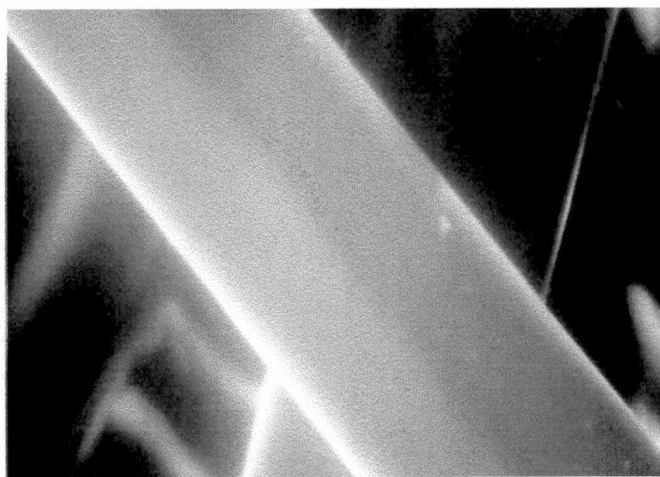
3.2 Scanning Electron Microscopy (SEM)

The surface geometry of the plasma treated PET and PP fibers as well as their controls was observed through scanning electron microscopy. The SEM images of plasma treated PET fibers were presented in Figure IV-11. It was noticed that the surface of untreated fiber was smooth and even [Fig. IV-11, a]. The similar surface of (N₂+H₂+He) plasma treated PET fiber was observed, although the treatment time varied from 15sec to 30 sec [Fig. IV-11, b, c]. On contrary, (SO₂+O₂) plasma caused the fiber a rough surface, scale-like substance appeared and likely increased in size with the plasma treatment time [Fig. IV-11, d, e]. It demonstrated that (SO₂+O₂) plasma was more energetic than (N₂+H₂+He) plasma. This modified surface was believed the essential factor of the improved dyeability of PET SB fiber. It is not only because of its functionalization but also because of its greatly increased specific surface area. The bumpy surface seemingly provided the evidence that chain scission occurred during (SO₂+O₂) plasma operation. The extremely reactive free radicals of atomic and molecular oxygen were the main reason for the chain-break and most likely happened in the positions which were showed as follows:





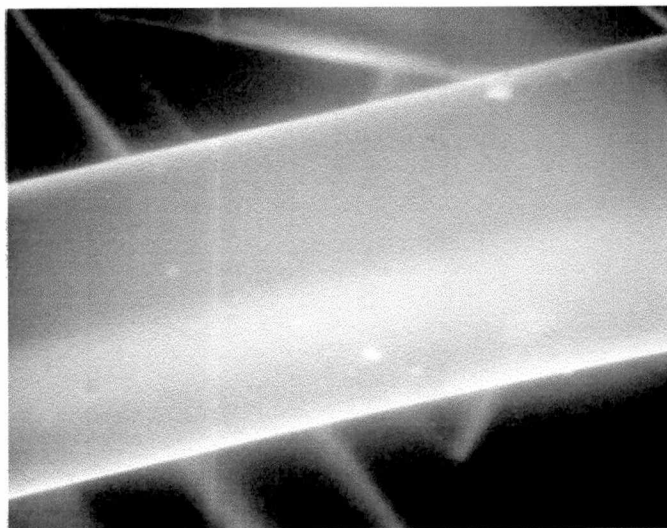
(a)



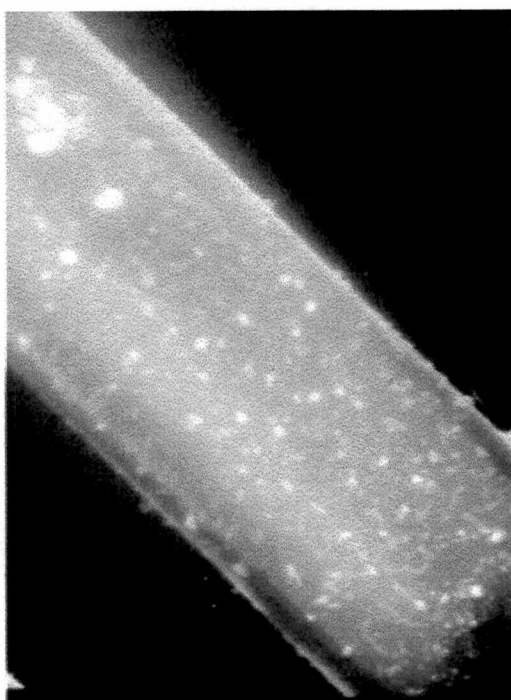
(b)

Figure IV-11 SEM Images of Plasma Treated PET SB Fibers

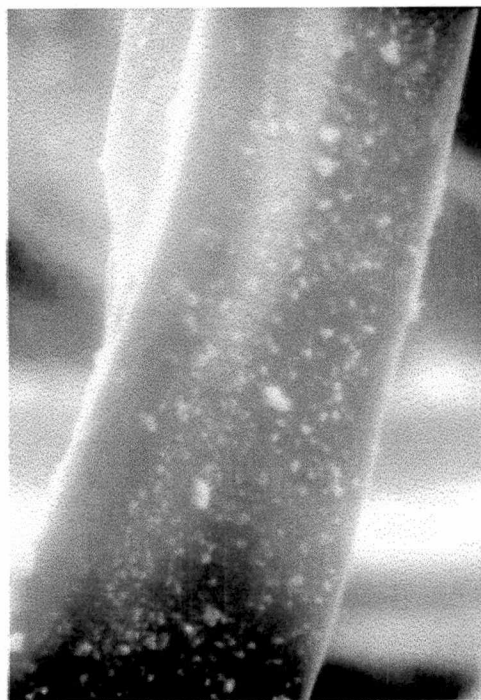
(a) control; (b) (N₂+H₂+He) Plasma, 15 sec; (c) (N₂+H₂+He) Plasma, 30 sec;
 (d) (SO₂+O₂) Plasma, 10 sec; (e) (SO₂+O₂) Plasma, 15 sec



(c)



(d)



(e)

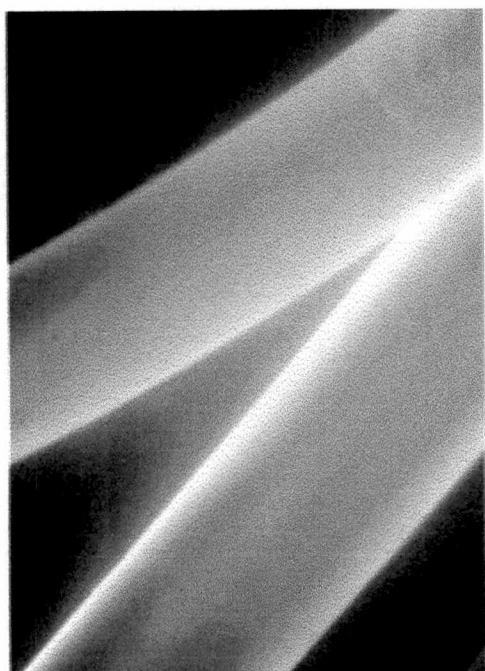
Figure IV-11 (continued)

Ultraviolet (UV) light is produced during plasma running. It was reported that UV light was one of the other reasons for polymer chain breakdown [76]. The SEM images of ($\text{N}_2+\text{H}_2+\text{He}$) plasma treated PET fiber suggested the UV light was not significantly important under the experiment conditions.

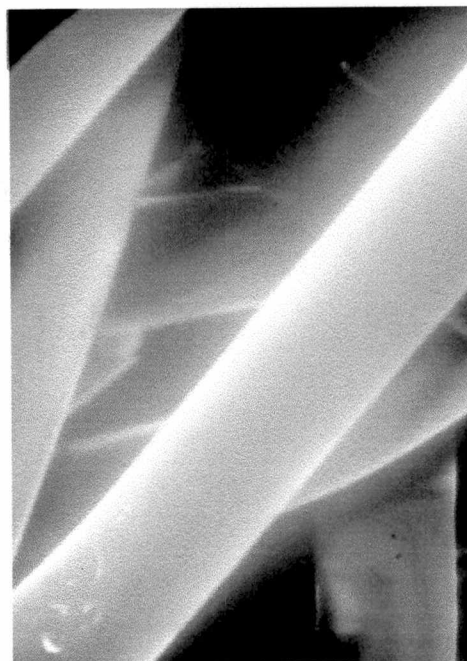
The surfaces of plasma treated PP fibers and their control were displayed in Figure IV-12. The ($\text{N}_2+\text{H}_2+\text{He}$) plasma did not significantly affect the topology of the PP fiber (Fig.IV-12 a, b, c). A significant surface change was produced by an atmospheric plasma using air as working gas. Many small and low cone-shaped bumps appeared on PP fiber surface [Fig.IV-12, d]. As treatment time increased, these bumps evidently became larger in size [Fig.IV-12, e] and finally combined together to form a totally disturbed surface [Fig.IV-12, f]. Thermal analysis was conducted and it was found that the crystallinity of PP fiber decreased with treatment time in air plasma [see Table IV-13]. Considering the SEM images, it seemed to suggest the air plasma caused the chain scission, which produced polypropylene with lower molecular weight and enable the surface more sensitive to heat. Under heat, these relatively small molecules achieved higher mobility and perturbed the crystal structure in the surface region, which caused the crystallinity decrease. In air plasma, many parts of the surface were oxidized and the function groups were introduced [see Chapter IV, Section 3.3]. The area with polar groups has higher surface tension (surface energy) and drew the mobile molecule fragments from all directions, which responded the formation of the cone-shaped bumps. In the case of (SO_2+O_2) plasma treated PET, the bumps



(a)

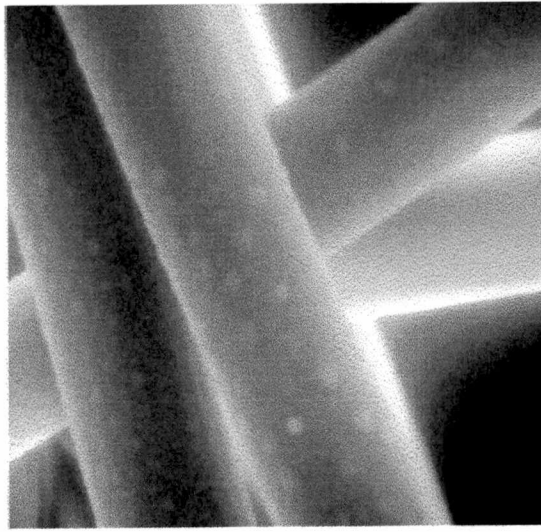


(b)

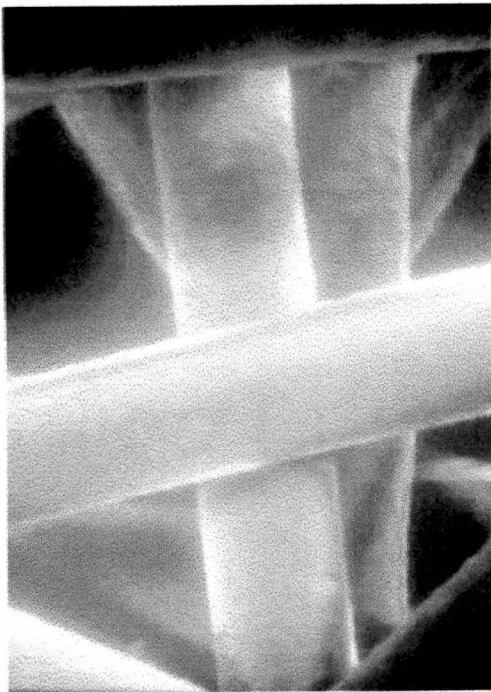


(c)

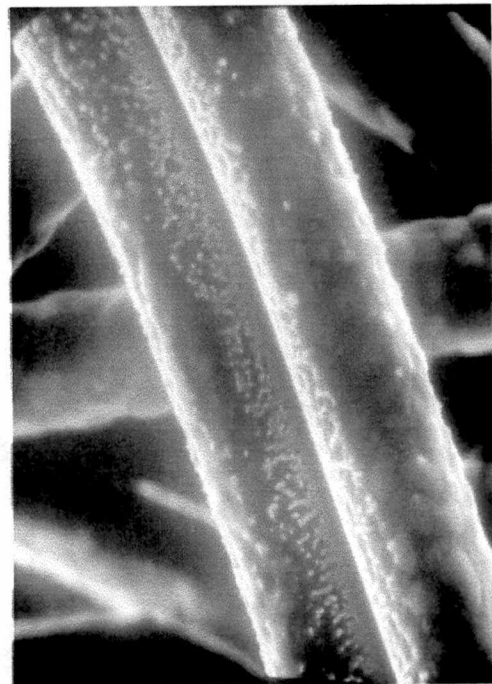
Figure IV-12 SEM of Plasma Treated PP SB Nonwoven Fibers
(a) Control; **(b)** ($\text{N}_2+\text{H}_2+\text{He}$) Plasma, 15 sec; **(c)** ($\text{N}_2+\text{H}_2+\text{He}$) Plasma, 30 sec;
(d) Atmospheric Air Plasma, 30 sec; **(e)** Atmospheric Air Plasma, 60 sec;
(f) Atmospheric Air Plasma, 300 sec



(d)



(e)



(f)

Figure IV-12 (continued)

showed different shape, which is likely because the hydrogen bonds among the chains prevent the migration of the molecular fragments.

3.3 Fourier Transition Infrared Spectroscopy (FTIR)

In order to detect the surface chemical variation after plasma treatment, a preliminary research was carried out. In this work, PET and PP spunbond nonwoven webs were treated with different working gas plasma, i.e. PET webs were treated with (SO₂+O₂) plasma and PP webs were treated with (N₂+He+H₂) and atmospheric plasma using air as working gas.

The photoacoustic (PA) infrared spectrum of PET treated with (SO₂+O₂) plasma was presented in Figure IV-13. The IR spectroscopy data indicated that (SO₂ + O₂) plasma induced composition change on fiber surface and proved longer treatment time resulted in more modifications.

The sharp band located at $\sim 3425\text{ cm}^{-1}$ is due to the stretching mode of free hydroxyls (ν O-H) [Fig IV-13]. After plasma treatment, its relative intensity decreased with treatment time [Fig. IV-13 b, c], which indicated the amount of hydroxyls were increased on the fiber surface and hydrogen bonds were developed among these groups. The stretching of hydrogen-bonded hydroxyl is associated with $3200\sim 3400\text{ cm}^{-1}$, whose intensity increment was a support to the above argument.

The bands in the region of $1680\sim 1780\text{ cm}^{-1}$ in Figure IV-13 were due to various carbonyls such as ester carbonyl (1720 cm^{-1}), carboxyl carbonyls ($1690\sim 1715\text{ cm}^{-1}$), and ketone & aldehyde carbonyls ($1700\sim 1715\text{ cm}^{-1}$) [78]. Although they are the strongest bonds in the spectra, they are almost useless in this work because of the small change in

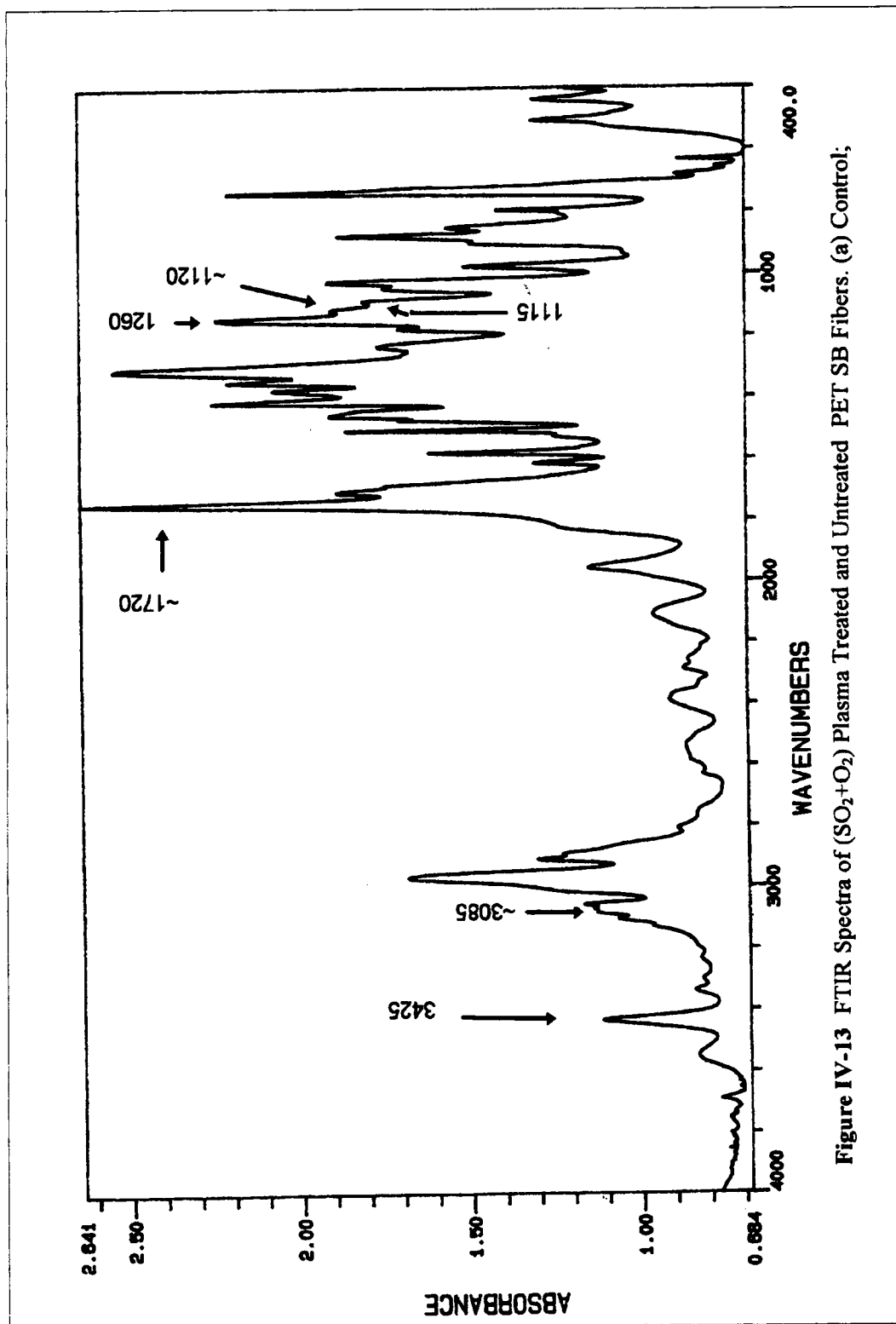


Figure IV-13 FTIR Spectra of (SO₂+O₂) Plasma Treated and Untreated PET SB Fibers. (a) Control;

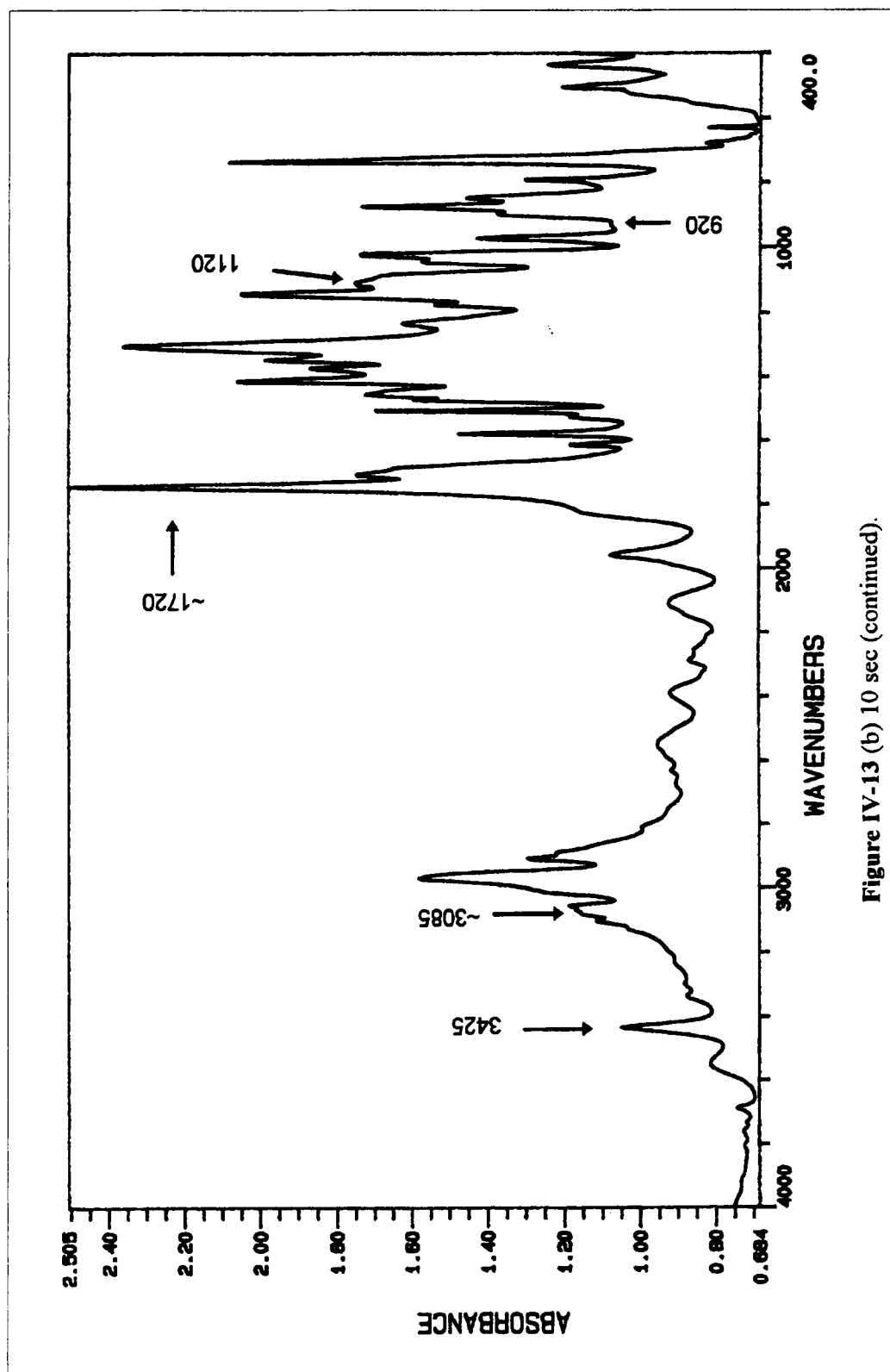


Figure IV-13 (b) 10 sec (continued).

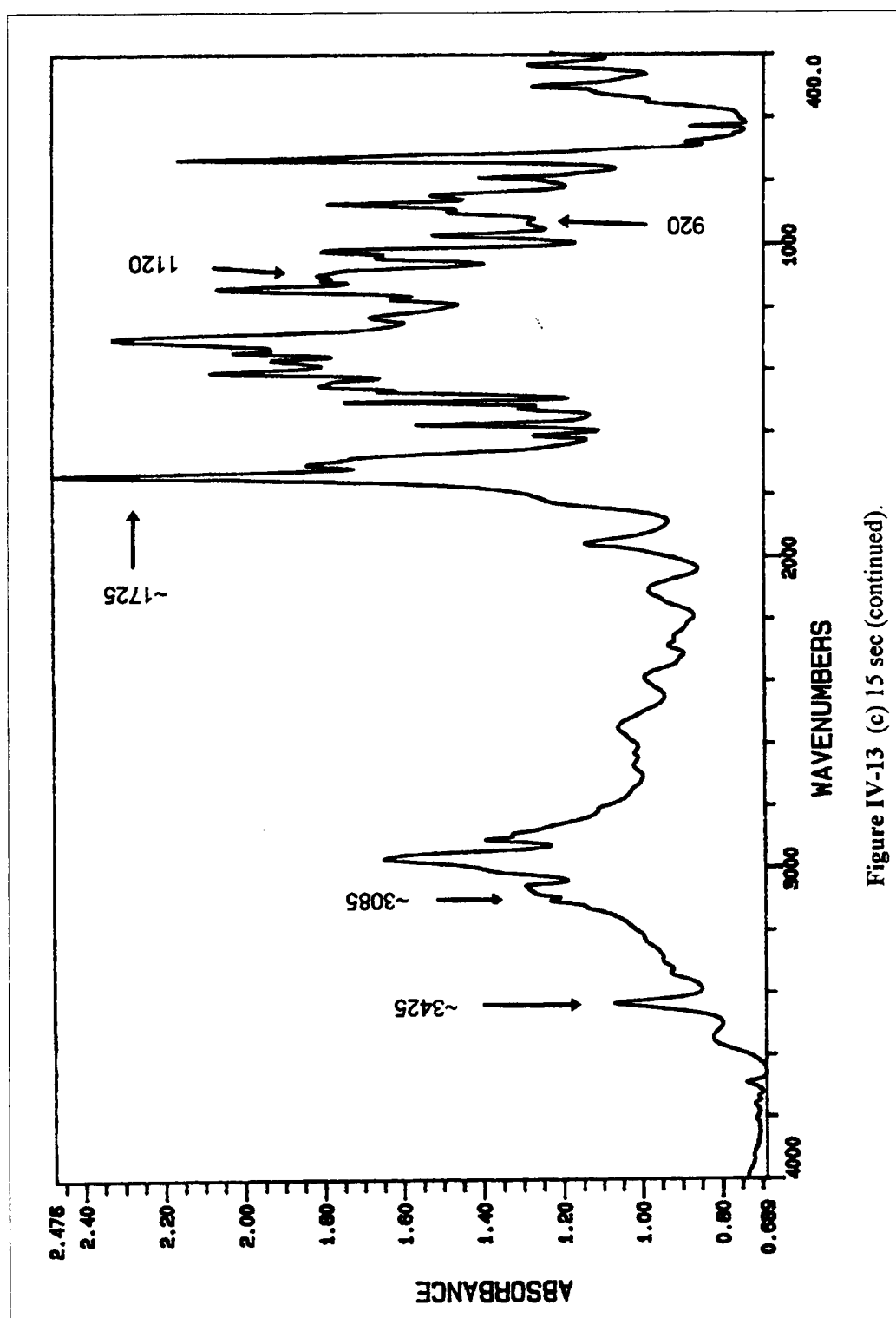


Figure IV-13 (c) 15 sec (continued).

their strengths before and after plasma treatment. The bands in 1260 cm^{-1} and 1120 cm^{-1} are due to the stretching of carbon-oxygen bond in the aromatic ester groups [Fig. IV-13, a]. The bands in 1115 cm^{-1} in Figure IV-13 b and c were associated with the stretching vibration of the sulfur- oxygen double bonds ($\nu\text{ S=O}$). It was believed that they were overlapped with other bands in this region. Similarly, the band in 920 cm^{-1} was an overlapped peak, which partially due to the stretching mode of the sulfur-oxygen bond ($\nu\text{ S-O}$).

The free hydroxyl band intensity at 3425 cm^{-1} and the S-O band intensity at 920 cm^{-1} were normalized against the band intensity at 3085 cm^{-1} , which is associated with the carbon-hydrogen stretching for the aromatic rings. The data were presented in Table IV-10. It was noticed that the intensities of the bands in 920 cm^{-1} increased with plasma treatment time. The results demonstrated that sulfur-oxygen-containing functional groups were introduced on to the fiber surfaces, even though identifying the group type based on these results would be difficult.

The PA infrared spectrum of PP treated with ($\text{N}_2+\text{He}+\text{H}_2$) plasma was shown in Figure IV-14. The IR spectroscopy data did not indicate the chemical change on fiber surface, but the result of dyeing experiments showed the improved dyeability [see Chapter IV, Section 1]. It was obvious that the further research was needed to verify if chemical changes happened on PP fiber surface after ($\text{N}_2+\text{He}+\text{H}_2$) plasma treatment.

The PA-IR spectra of PP treated with air atmospheric plasma are presented in Figure IV-15. It demonstrated that significant chemical changes occurred on PP fiber surface. The broad band appeared in the frequency region of $1715\text{-}1780\text{ cm}^{-1}$ is due to the various carbonyls, including ketone and aldehyde carbonyl, carboxyl carbonyl,

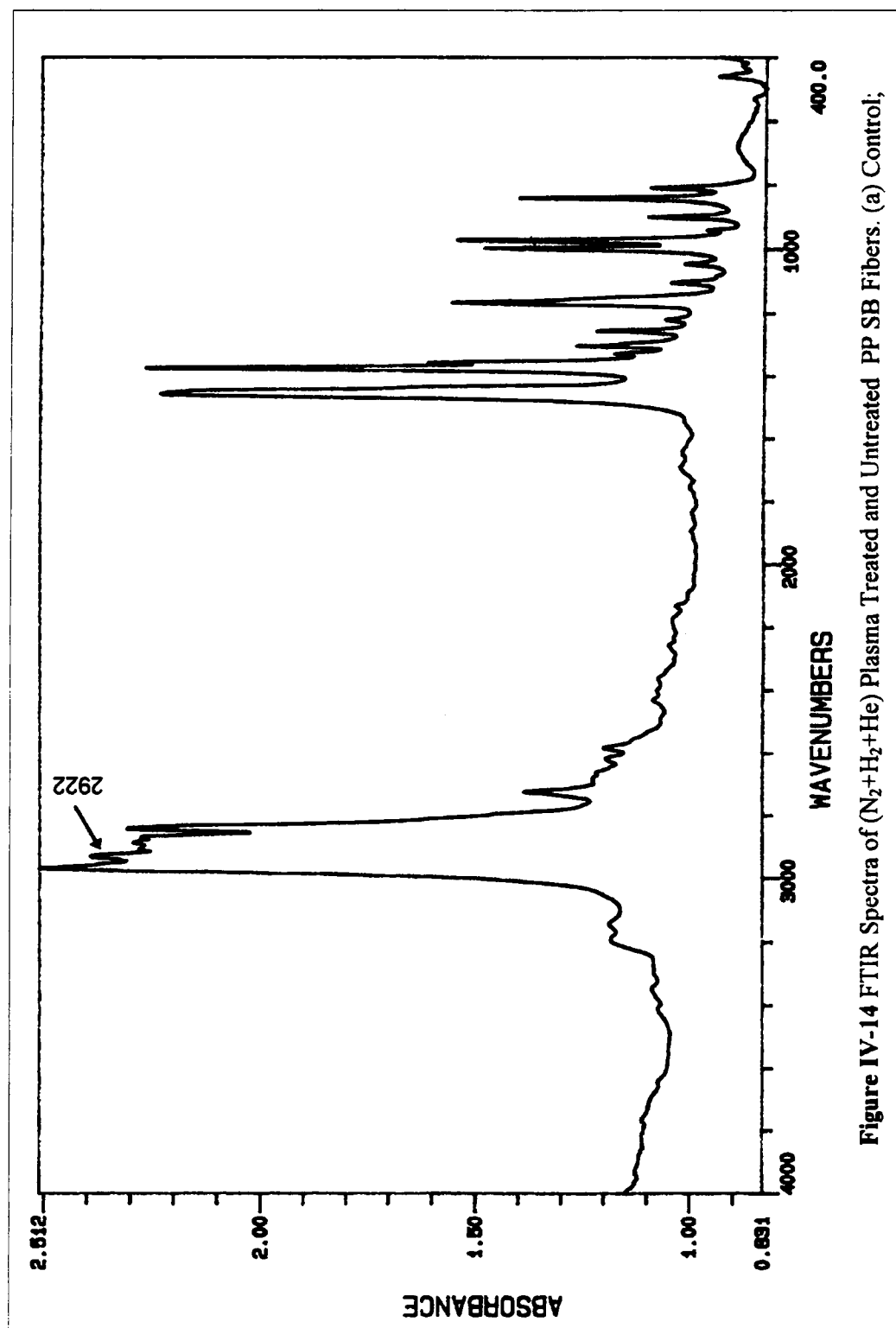


Figure IV-14 FTIR Spectra of (N₂+H₂+He) Plasma Treated and Untreated PP SB Fibers. (a) Control;

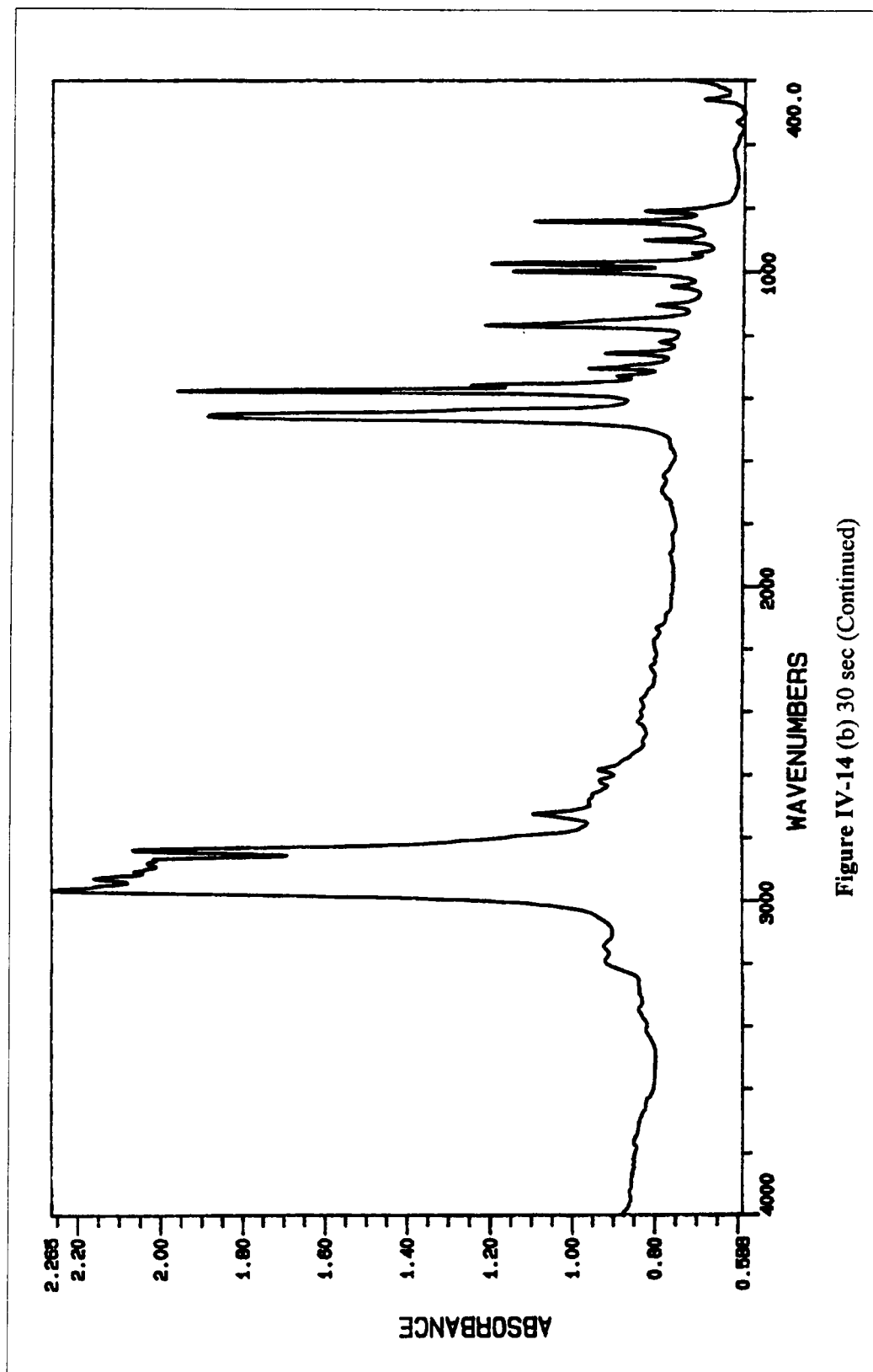


Figure IV-14 (b) 30 sec (Continued)

Table IV-10 Relative Intensity of Selected Bands in the PA-FTIR Spectra of PET

Treatment time (sec)	Relative Intensity ¹	
	ν O-H in 3425 cm^{-1}	ν S-O in 920 cm^{-1}
0	94.06	88.13
10	87.87	90.37
15	82.31	99.23

Note: Normalized against the band intensity at 3085 cm^{-1} and its intensity was assumed 100. PET were treated with ($\text{SO}_2 + \text{O}_2$) plasma.

ester carbonyl and anhydride carbonyl that formed during air plasma treatment. This band was believed to be an overlapped band of more than one of above listed peaks. The broad band in $3100\sim 3600\text{ cm}^{-1}$ is associated with the stretching mode of hydrogen bonded hydroxyl [Fig.IV-15, d], which indicated that alcohol /peroxide was formed during air plasma treatment.

Normalized against the band at 2922 cm^{-1} , which is due to the asymmetric stretching of methylene in the polypropylene molecules, the carbonyl band intensities for different treatment times were presented in Figure IV-16. It was clearly exhibited that plasma treatment time is closely related with the density of the carbonyl groups. Surface oxidation is enhanced as plasma treatment time increased, which produced more polar carbonyls. It also showed that there seemed an initial stage for surface oxidation during plasma treatment. A similar phenomenon was noticed by Dr. Yong [78]. With respect to the band of hydroxyl in $3100\sim 3600\text{ cm}^{-1}$ [Fig. IV-15, c, d], it may be not proper to jump to the conclusion that the hydroxyl groups were not formed until treatment time was long

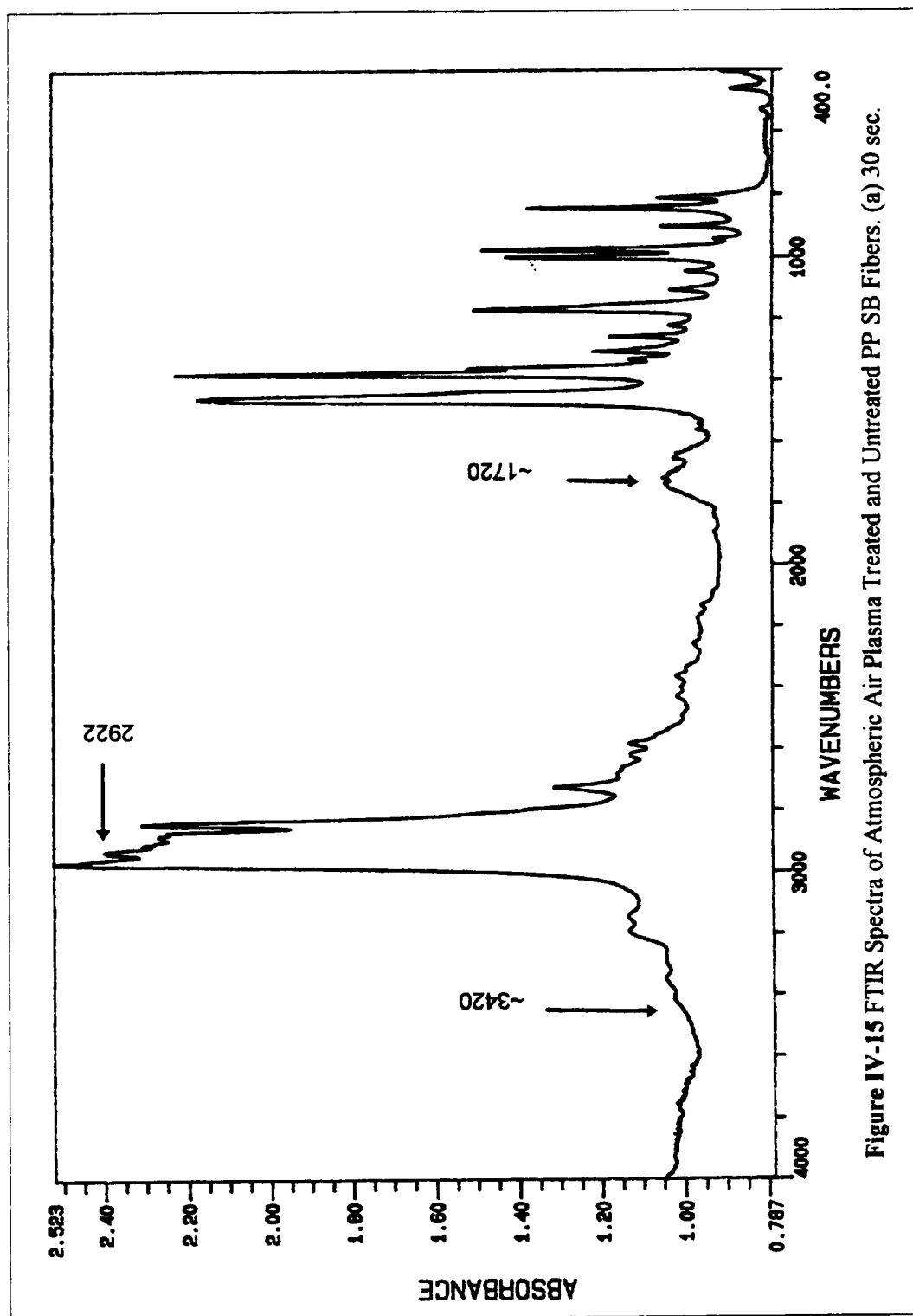


Figure IV-15 FTIR Spectra of Atmospheric Air Plasma Treated and Untreated PP SB Fibers. (a) 30 sec.

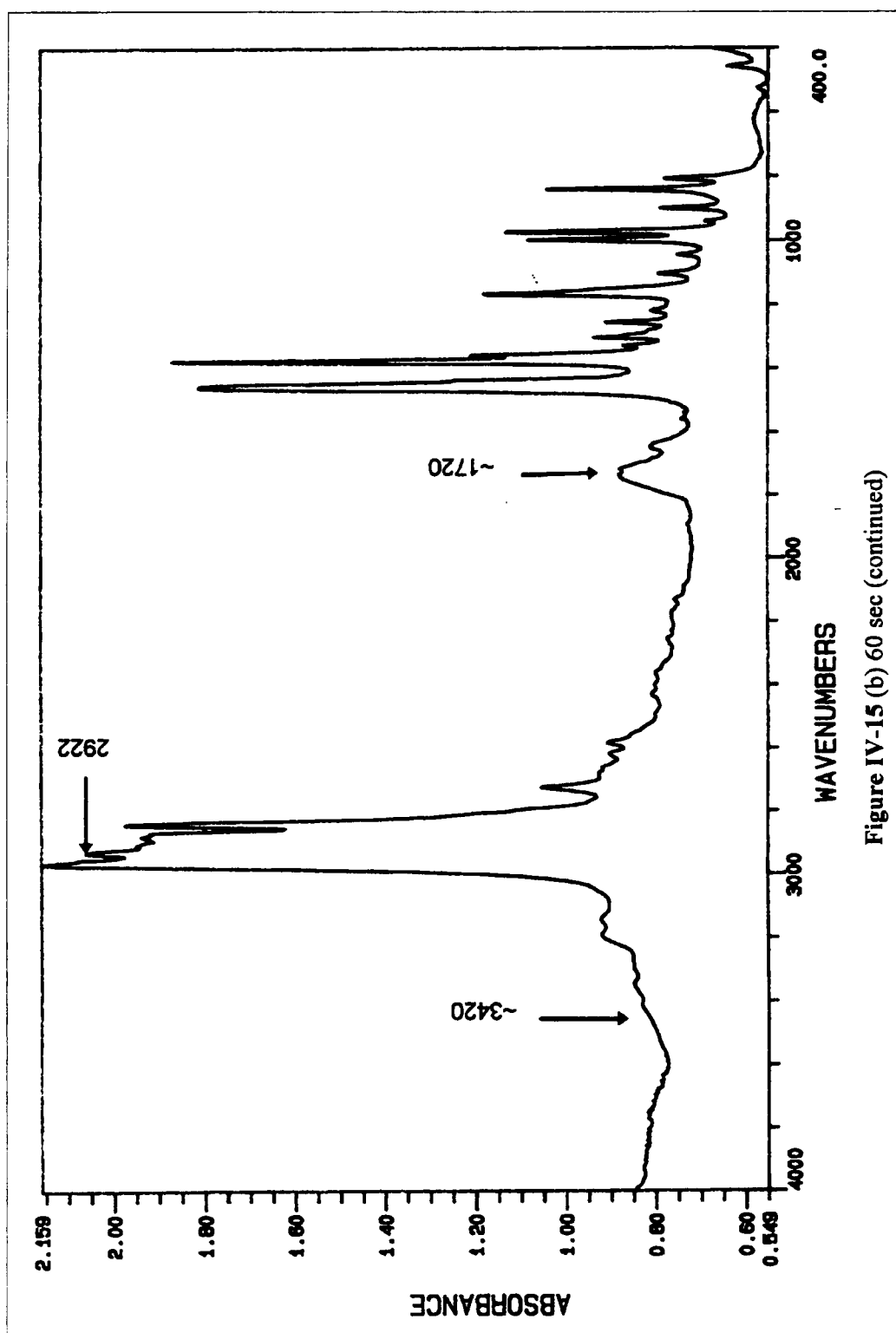


Figure IV-15 (b) 60 sec (continued)

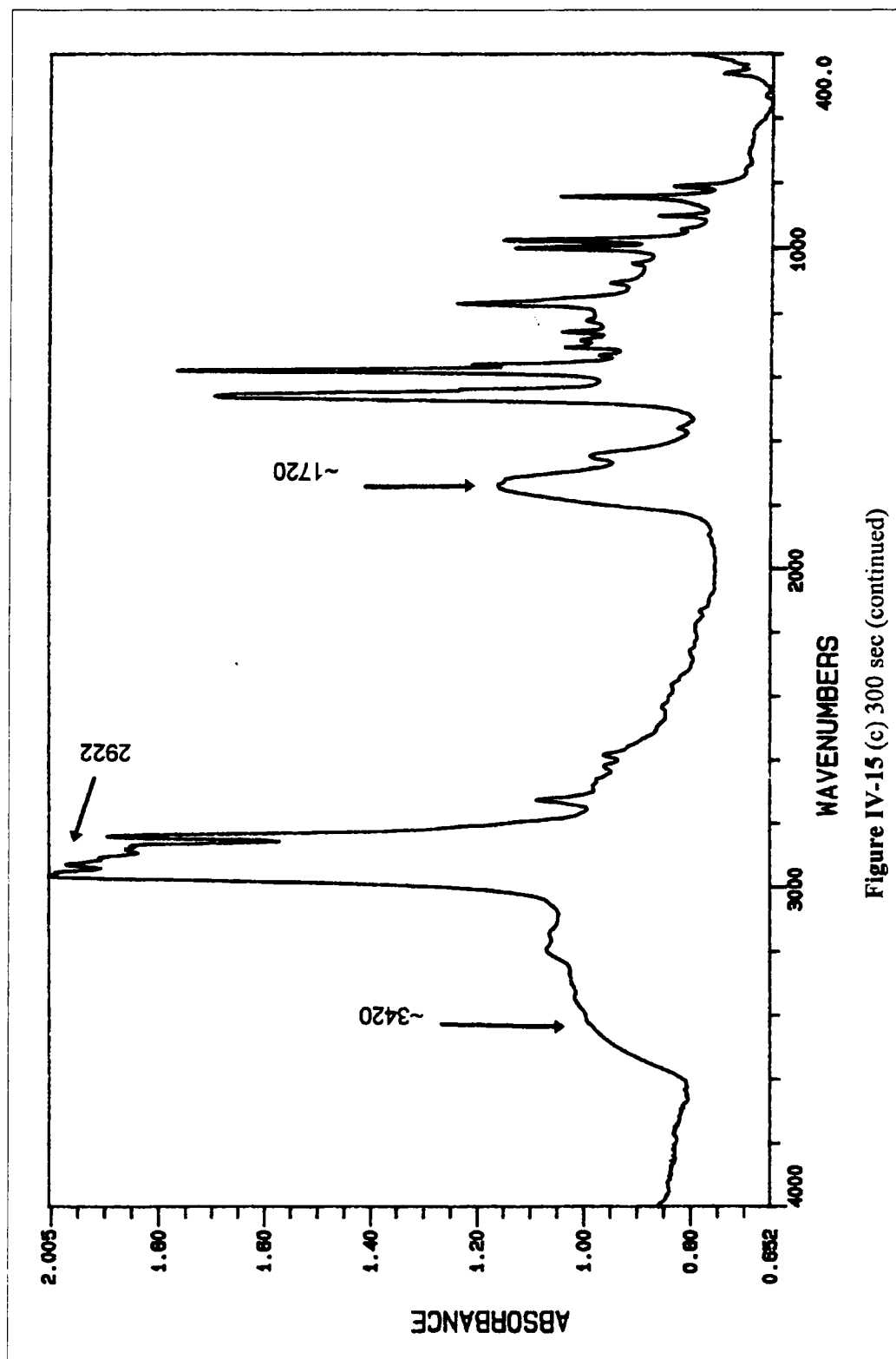


Figure IV-15 (c) 300 sec (continued)

enough, because the band of hydrogen-bonded hydroxyl is usually broad and weak. Considering the composition of air, the nitrogen containing groups were expected be implanted on PP fiber surface also. No significant signals shown in the spectrum of Figure IV-15. This result proved that oxygen plasma was much active and the FTIR is a powerful tool for oxygen containing functionalities. Once again it may be harmful to conclude that there was no nitrogen containing groups introduced on to that PP fiber surface. Further research on this issue is suggested by using other surface analysis techniques that are more sensitive to nitrogen element, such as Electron Spectroscopy for Chemical Analysis (ESCA).

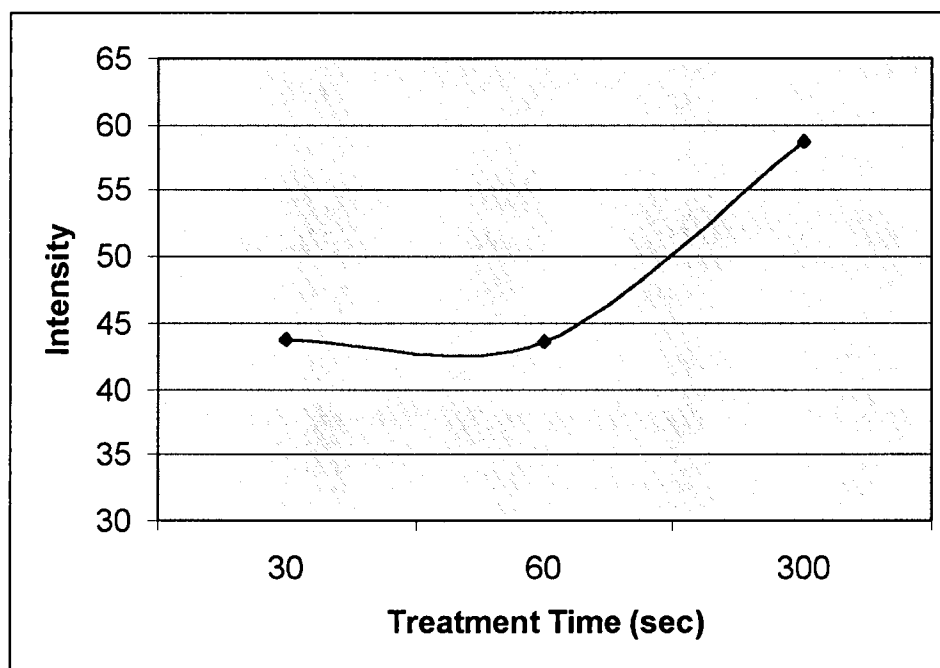


Figure IV-16 The Relationship Between Air Plasma Treatment Time and Carbonly Band Intensity (Atmospheric Plasma treatment in Air, PP SB nonwoven Web)

4. Tensile Property of Plasma Treated PET and PP SB Webs

It was reported in literature [15] that plasma treatment might not affect the mechanical properties of the fibers, which was based on the fact that plasma treatment is a superficial technique. Under some special conditions, the above statement may not be reliable. In this research, data shown in Table IV-11 suggested the given plasma influenced the mechanical properties of the spunbond nonwoven webs, such as break elongation and initial modulus. (SO_2+O_2) plasma decreased the initial modulus of PET nonwoven webs, whereas ($\text{N}_2+\text{H}_2+\text{He}$) plasma increased the initial modulus, even though the changes seem to be small. Because only the surface of the fiber was affected, it might be proper to consider this change significant.

The reasons why different plasma affects the mechanical properties in different directions are not clear in literature. The following reasons were proposed based on the understanding of the principles of the plasma treatment and plasma chemistry. Further research is obviously required to give more evidence in order to support these discussions.

The (SO_2+O_2) plasma produced comparatively more reactive species. These oxygen-containing and sulfur-oxygen-containing active species have more kinetic energy compared to N_2 -containing species due to their relatively higher atomic mass of oxygen and sulfur atoms. Higher kinetic energy allows the active species collide with polymer molecular chains more efficiently, which results in the higher probability of scissoring the macromolecular chains. But most importantly, the chemical activity allows the species both successfully implant functional groups on the fiber surfaces and breakdown the macromolecular chains.

**Table IV-11. Effect of Plasma Treatment on the Mechanical Properties of
Spunbond PET Nonwoven Webs**

SAMPLES	PLASMA CONDITIONS		BREAK ELONGATION (%)	INITIAL MODULUS (N/TEX)
0110PET- III-1	3* SO ₂ + 0.1* O ₂ P=400/75 (325W) T=102°F, p=696 Torr	10sec	19.63	0.303
0110PET III-2		15sec	20.38	0.304
0110PET -III-3	10*N ₂ +1.5*He +0.25*H ₂ P=350/50 (300W) T=85°F, p=696 Torr	30sec	20.80	0.352
0110PET -III-4		15sec	25.65	0.358
Control PET	-----		17.82	0.319

Broken chains also create more weak points of fiber surfaces. Macromolecular chain scission caused by (SO₂+O₂) plasma might be the main reason of the decreased web initial modulus. As shown in Figure IV-11 b and c, the (SO₂+O₂) plasma treated PET fibers had rough surfaces, which seemed to support the above argument.

The (N₂+He+H₂) plasma, on the contrary, increased the initial modulus of PET fiber, which might result from crystallinity increase [see Table IV-3]. Under the given conditions, active species created by (N₂+He+H₂) plasma are relative less powerful, their energy is not high enough to cut the molecular chains [See Fig.IV-11, b & c]. Without plasma caused weak points, the increased crystallinity could partially explain the result of Table IV-11. In addition, plasma active species can create free radicals along the fiber molecular chains,

although they can not break them. Two or more of them may react with each other so that cross-linking occurs. This may be the other reason. The increased elongation seems to be associated with this assumption.

The tensile testing data of ($\text{N}_2+\text{H}_2+\text{He}$) plasma treated PP SB web were presented in Table IV-12. The decreasing trends in both break elongation and initial modulus were noticed. This phenomenon is different from that of PET webs. Because SEM photograph suggested little chain scission [Fig. IV-12 a, b & c], the plasma must changed other properties of PP web. DSC Analysis showed their crystallinities were decreased during plasma treatments [Table IV-13], This may to some degree explain the data in Table IV-12. Because of the nature of fast crystallization rate, molten PP rapidly develops its crystalline right after extruded out. Its flexible molecular chains allow high crystallinity even without drawing. Although the plasma active species transfer energy to the fiber surfaces and may raise fiber surface temperature, the crystallinity could not increase because it is already well developed.

Table IV-12 Effect Of Plasma Treatment on the Mechanical Properties of Spunbond PP Nonwoven Webs

SAMPLES	PLASMA CONDITIONS		BREAK ELONGATION (%)	INITIAL MODULUS (N/TEX)
0109PP I 1	10* N ₂ + 0.25* H ₂ P=500/50 (450W) T=71°F, p=696 Torr	5sec	24.58	0.39
0109PP I 2		30sec	22.51	0.39
0110PP II 2	10*N ₂ +1.5*He +0.25* H ₂ P=400/25 (375W) T=91°F, p= 696 Torr	10sec	14.99	0.49
0110PP II 3		15sec	11.83	0.47
Control PP			34.60	0.51

* Note: gas flow rate in L/min

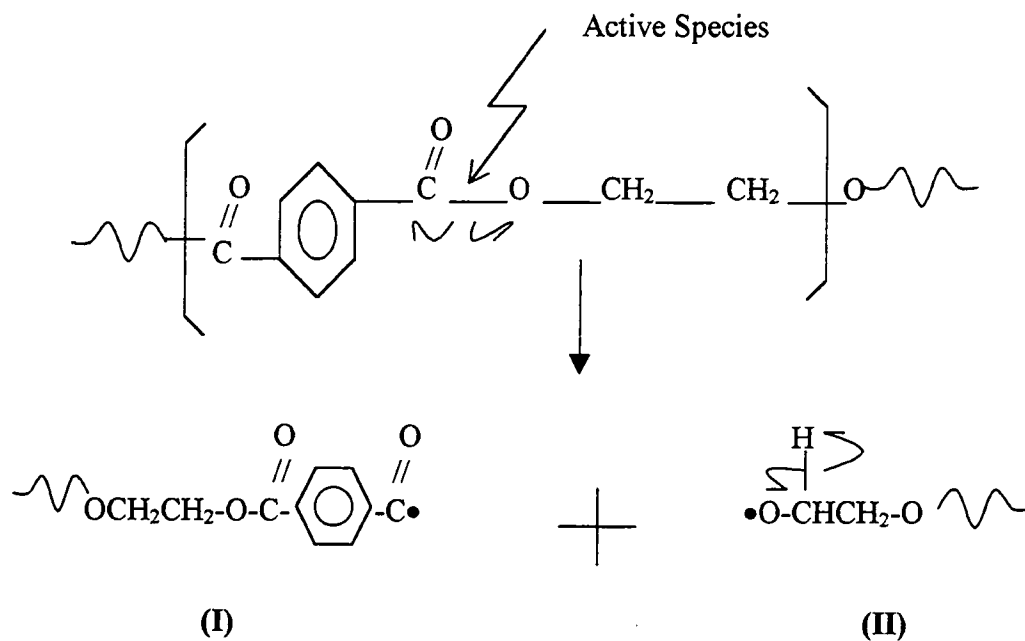
Table IV-13. Effects Of Plasma Treatment on Crystallinity of PP Nonwoven Fibers

SAMPLES	PLASMA CONDITIONS		ΔH s (J/G)	CRYSTALLINITY (%)
0110PP II-1	10*N ₂ +1.5*He +0.25*H ₂ P=400/25 (375W) T=91°F, p=696 Torr		----	-----
0110PP-II-2		10sec	76.2	46.18
0110PP-II-3		15sec	70.7	42.85
0629PP-III-1	Gas: Air Freq. = 6.0 kHz Volt. = 5.8 kV Pressure = 1 atm. Current =800μA	30sec	76.6	46.42
0629PP-III-2		60sec	74.7	45.27
0629PP-III-3		300sec	69.3	42.00
Control PP			77.6	47.03

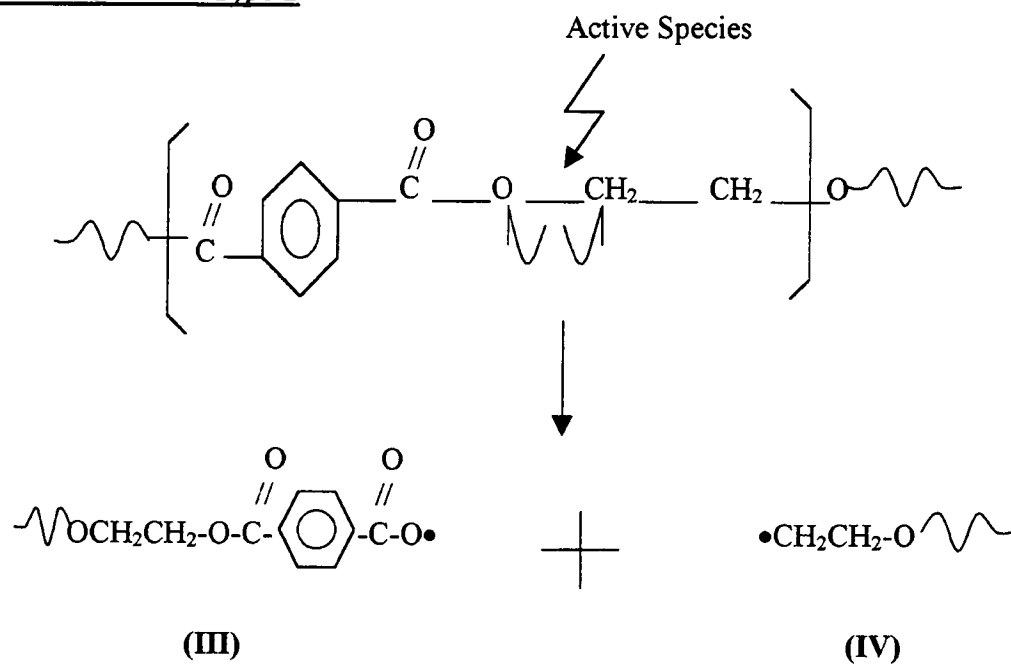
Note : ΔH_∞ = 165 J/g [83]

5. A Possible Mechanism of Plasma Functionalization for PET Fiber

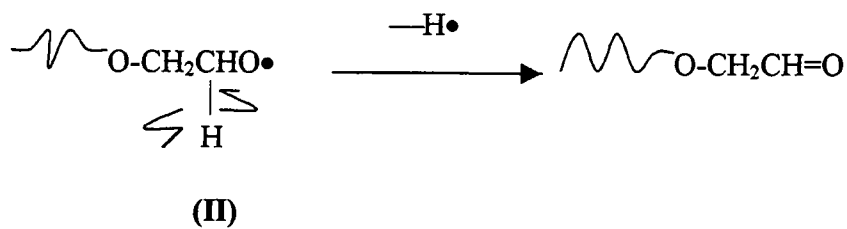
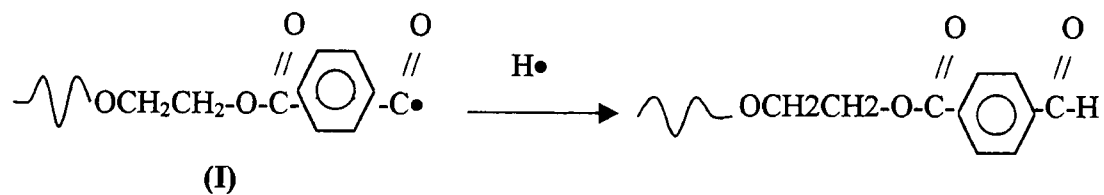
Chain Scission: Type 1



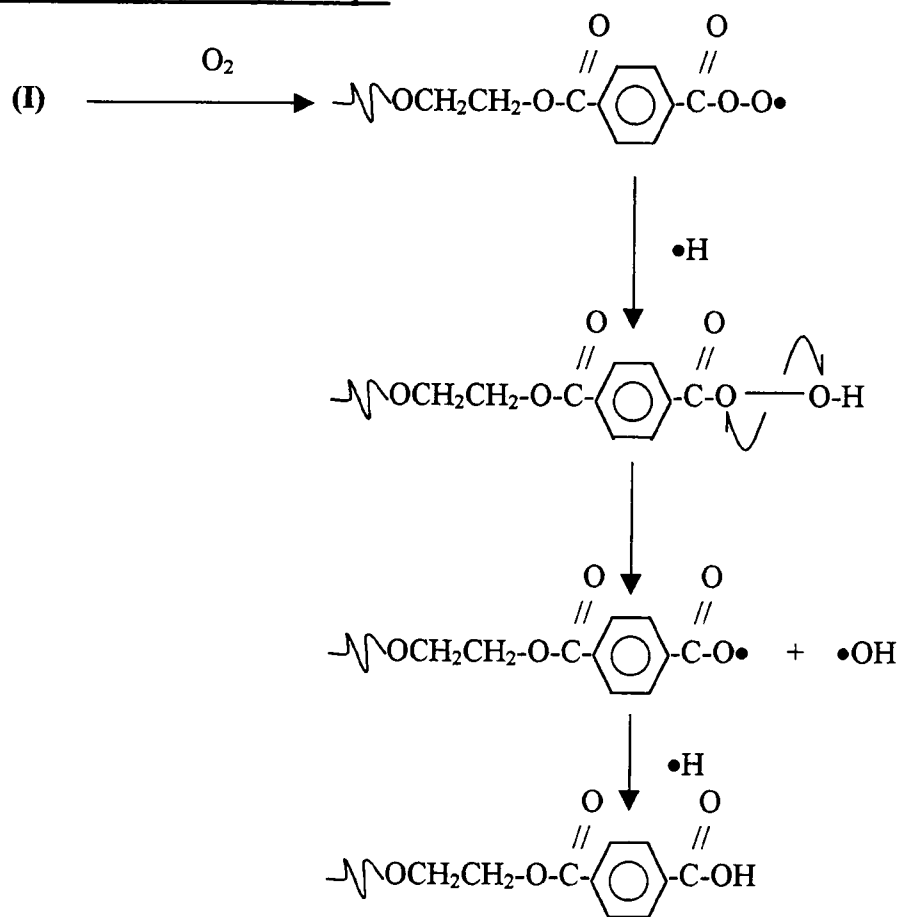
Chain Scission: Type 2

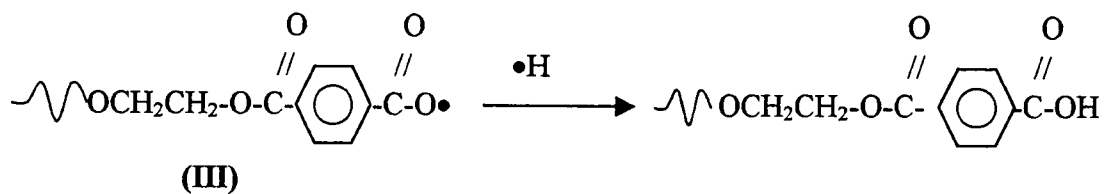


The Formation of Carbonyl Groups

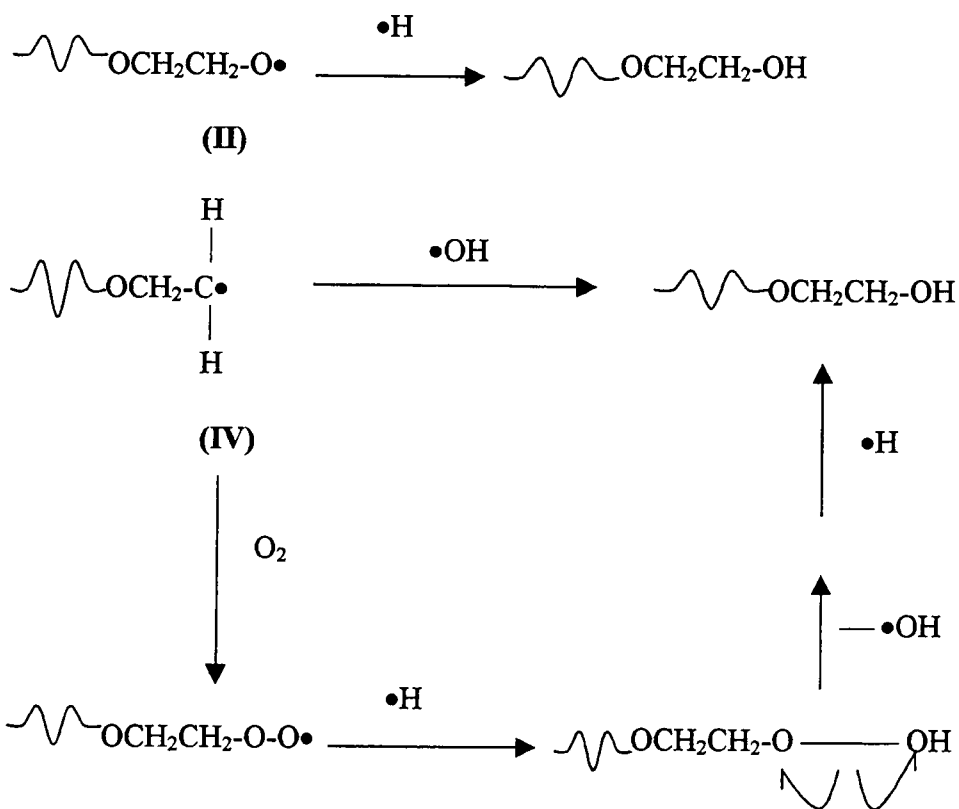


The Formation of Carboxyl Groups

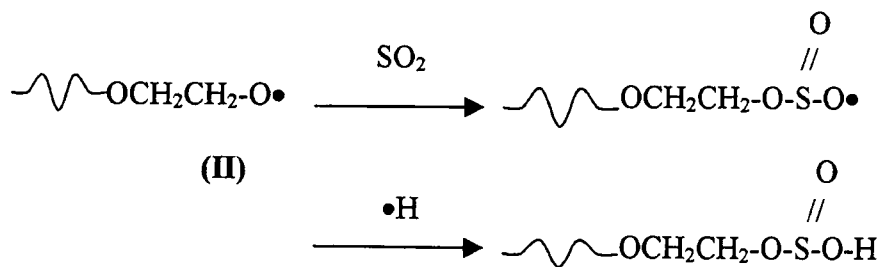




The Formation of Hydroxyl Groups



The Formation of Sulfo Groups



V. CONCLUSIONS

1. Plasma treatment provided a promising tool for surface modification of spunbond (SB) nonwoven fabrics. (SO_2+O_2) plasma and ($\text{N}_2+\text{H}_2+\text{He}$) plasma significantly improved the dyeability of PET spunbond nonwoven web. They implanted functional groups onto the fiber surface, which give the fabrics affinity to both water and water soluble dyes.
2. For the water-soluble acid dye, the functional groups served as active sites, through which the dye molecules were attracted to the fibers. Although the increased crystallinity after plasma treatment could potentially decrease dyeability of PET, the implanted functionalities played the predominant role in improving dyeability.
3. It was shown that (SO_2+O_2) plasma treated PET spunbond nonwoven web could be dyed using traditional water-soluble acid dye. A pH value of 4.77, dyeing temperature of 172°F and dyeing time of 60 min are the preferred dyeing conditions.
4. The PET SB fiber demonstrated a "Skin-Core" type structure after (SO_2+O_2) plasma treatment. The "Skin" is a polarized layer with many functional groups and is approximately 1.8 microns in thickness. The "Core" is the inner of fiber without plasma affect. The "Skin" layer is the key in improving dyeability of fabrics and durability of plasma treatment.
5. The ($\text{N}_2+\text{H}_2+\text{He}$) plasma also significantly improved the dyeability of PP spunbond nonwoven webs. As would be expected the plasma treatment of PP web is less successful than that of PET.

6. The plasma with oxygen-containing working gas is more powerful than that without oxygen-containing working gas.
7. Differential scanning calorimetry analysis showed that plasma treatment increased the crystallinity of PET spunbond fiber, but decreased that of PP SB fiber.
8. Fourier transform infrared spectroscopy (FTIR) indicated oxygen containing functional groups were introduced onto fiber surface after ($\text{SO}_2 + \text{O}_2$) plasma treatment. In this research, FTIR did not successfully demonstrate the presence of nitrogen containing functional groups on fiber surface.
9. The evidence of surface molecular chain scission caused by oxygen containing plasma was observed through Scanning Electron Microscopy.
10. Plasma treatment affects the mechanical properties of PET and PP fiber in different ways depending on different plasma conditions. Oxygen-involved plasma potentially decreased the fiber strength due to chain scission. Nitrogen-containing plasma (without Oxygen containing gas) seemingly increased the PET fiber strength but slightly decreased the strength of PP fiber.

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APPENDIX

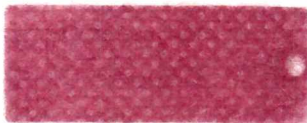
Appendix 1

Dyeing of (SO ₂ +O ₂) Plasma Treated PET SB Webs with Acid Red (pH=4.77, Dyeing Temp.=172°F)				
Dyeing Time (min)	PET-1 (10 sec)	PET-2 (15 sec)	Control	
15				
30				
45				
60				

Dyeing of (SO ₂ +O ₂) Plasma Treated PET SB Webs with Acid Blue (pH=4.77, Dyeing Temp.=172°F)				
Dyeing Time (min)	PET-1 (10 sec)	PET-2 (15 sec)	Control	
15				
30				
45				
60				

Appendix 3

Coloration of Plasma treated Spunbond PET Nonwoven Webs by Acid Dyes

Plasma Treatment Conditions	Acid Red	Acid Blue
Working gases: $3 * SO_2 + 0.1 * O_2$ Power: $P = 400/75$ Temperature: $T = 102^{\circ}F$ Pressure: $P = 27.4 \text{ "Hg}$	0110PET-III-1 10 sec 	0110PET-III-1 10 sec 
	0110PET-III-2 15 sec 	0110PET-III-2 15 sec 
	0110PET-III-3 30 sec 	0110PET-III-3 30 sec 
Working gases: $10 * N_2 + 1.5 * He + 0.25 * H_2$ Power: $P = 350/50$ Temperature: $T = 85^{\circ}F$ Pressure: $P = 27.4 \text{ "Hg}$	0110PET-III-4 15 sec 	0110PET-III-4 15 sec 
	0110PET-III-5 10 sec 	0110PET-III-5 10 sec 
	0109PET 5 sec 	0109PET 5 sec 
Control		

Note: * gas flow rate in L/min

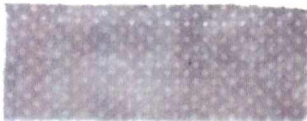
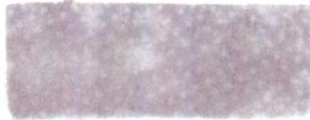
Appendix 4

Coloration of Plasma treated Spunbond PET Nonwoven Webs by Basic Dyes

Plasma Treatment Conditions	Basic Red	Basic Blue
Working gases: $3 * SO_2 + 0.1 * O_2$ Power: $P = 400/75$ Temperature: $T = 102^{\circ}F$ Pressure: $P = 27.4 \text{ "Hg}$	0110PET-III-1 10 sec 	0110PET-III-1 10 sec 
	0110PET-III-2 15 sec 	0110PET-III-2 15 sec 
Working gases: $10 * N_2 + 1.5 * He + 0.25 * H_2$ Power: $P = 350/50$ Temperature: $T = 85^{\circ}F$ Pressure: $P = 27.4 \text{ "Hg}$	0110PET-III-3 30 sec 	0110PET-III-3 30 sec 
	0110PET-III-4 15 sec 	0110PET-III-4 15 sec 
	0110PET-III-5 10 sec 	0110PET-III-5 10 sec 
Working gases: $5 * N_2 + 0.25 * H_2$ Power: $P = 525/50$ Temperature: $T = 82^{\circ}F$ Pressure: $p = 27.4 \text{ "Hg}$	0109PET 5 sec 	0109PET 5 sec 
Control		

Note: * gas flow rate in L/min

Appendix 5
Coloration of Plasma treated Spunbond PP Nonwoven Webs

Plasma Treatment Conditions	Acid Blue	Acid Red
Working gases: $10^* \text{N}_2 + 0.25^* \text{H}_2$ Power: $P = 500/25$ Temperature: $T = 68^\circ\text{F}$ Pressure: $P = 27.4 \text{ "Hg}$	0110PP-I 30 sec 	
		
Working gases: $10^* \text{N}_2 + 2^* \text{He} + 0.25^* \text{H}_2$ Power: $P = 400/25$ Temperature: $T = 89^\circ\text{F}$ Pressure: $P = 27.4 \text{ "Hg}$	0110PP-II-1 30 sec 	
	0110PP-II-3 15 sec 	
	0110PP-II-2 10 sec 	
Working gases: $10^* \text{N}_2 + 4^* \text{H}_2 + 2\text{He}$ Power: $P = 500/50$ Temperature: $T = 72^\circ\text{F}$ Pressure: $p = 27.4 \text{ "Hg}$	0109PP 5 sec 	
Control		

Note: * gas flow rate in L/min

VITA

Rongguo Zhao was born in Hebei Province, The People's Republic of China on November 25, 1966. He graduated from Beijing Institute of Clothing Technology (BICF) with Master Degree in Chemistry in July 1992. Thereafter, he joined the faculty of Chemistry Department at BICT up to August 1996. His research focused on the following projects:

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2. Synthesis of Cationic Surfactants and Their Applications as Softening and Antistatic Agents for PET Fabrics.
3. New Chelating Fibers: Preparation, Characterization and Applications.
4. Synthesis of Acidic Ion-exchange Fibers and Resins.
5. Formulation of PET High-speed Spinning Finish Oil.

He entered the University of Tennessee, Knoxville in August 1996. Besides the classes in Textile Department, he took "Industrial Plasma Engineering" in Electrical Engineering Department and "Polymer Chemistry" in Chemistry Department. After received his Master Degree in Textile Science in May 1998, he is presently continuing his studies to pursue his Doctorate of Human Ecology with a concentration of Textile Science. Rongguo Zhao is a member of Fiber Society and China Textile Association.