To the Graduate Council:

I am submitting herewith a thesis written by Yi-Xiang Zhang entitled " A Study For Improving Melt Blown Processing of Recycled Poly(ethylene terephthalate)." 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 Master of Science,with a major in Textile, Retailing and Consumer Science.

Gajanan Bhat

Gajanan Bhat, Ph.D. Major Professor

We have read this thesis
and recommend its acceptance:

Larry C. Wadsworth

Marcus Dover

Accepted for the Council:

Associate Vice Chancellor
and Dean of The Graduate School

A STUDY FOR IMPROVING THE MELT BLOWN PROCESSING OF RECYCLED POLY(ETHYLENE TEREPHTHALATE)

A Thesis

Presented for the

Master of Science

Degree

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Yi-xiang Zhang

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ABSTRACT

Three methods to improve the melt blown processing of post-consumer recycled poly(ethylene terephthalate) (PET) were explored: (1) using undried PET instead of dried PET; (2) blending recycled PET with other polymers; and (3) processing recycled PET at a higher temperature. The hydrolytic degradation occuring in the presence of moisture and heat, blending with PBT, blending with low I.V. PET, and the thermal degradation were expected to decrease the apparent viscosity of recycled PET during melt blown processing. Low viscosity contributes to production of quality webs, which have smaller fiber diameters, lower air permeability, and higher tenacity.

The webs produced from undried PET, which had more moisture (0.263%) than dried PET (0.00713%), had lower intrinsic viscosity, smaller fiber diameters, lower air permeability and higher tenacity than those produced from dried PET. The load-elongation curves of webs produced from undried and dried PET were different. The undried PET webs had greater initial modulus, which indicated that the webs produced from undried PET had a more compact web structure.

The recycled PET (I.V. = 0.82) was blended with either one of two grades of virgin PBT (I.V. = 0.88 and I.V. = 0.77) or a low molecular weight virgin PET (I.V. = 0.62). The webs produced from recycled PET blended with PBT had lower intrinsic viscosity, smaller fiber diameter, less air permeability and higher tenacity in the machine direction. The webs produced from recycled PET blended with low I.V. PBT showed

greater property changes than those produced from recycled PET blended with high I.V. PBT. On the other hand, the blending of low I.V. PET with recycled PET had lower intrinsic viscosity, smaller fiber diameters, less air permeability, higher filtration efficiency, greater tenacity, and exhibited greater shrinkage than 100% recycled PET. They were also thinner. It was also observed that the extent of change in the properties of the webs was proportional to the amount of low I.V. PET in the blend.

Two different ways of using higher processing temperatures were explored: (1) the die temperature was increased from 295 to 315 ^{o}C; and (2) the temperatures of heating zones in the barrel were gradually increased from zone 1 to zone 4 in addition to increasing the die temperature to 315 ^{o}C. By only increasing the die temperature, no notable property improvements were achieved over those webs produced from recycled PET processed at normal temperatures. The webs produced by the later method had smaller fiber diameters, lower thickness and air permeability and greater tenacity in the machine direction.

The effects of heat setting on the properties of melt blown webs were also studied to determine a more practical method to control the shrinkage of the melt blown PET webs. Through heat setting, shrinkage of webs was considerably reduced. The thickness was also reduced, resulting in more compact web structure. Tenacity in the machine direction increased when the webs were heat set at lower temperature for a short time. When heat setting temperature and time further increased, the tenacity in the machine direction decreased. The DSC results of webs before and after heat setting indicated an increase in the crystallinity of fibers due to heat setting.

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CHAPTER I

INTRODUCTION

The U.S. production of plastics experienced an average annual growth rate of 10.3% from 1958 to 1988 [1]. While plastics offer many advantages over traditional raw materials such as wood and glass i.e., design flexibility, strength, resistance to degradation and corrosion, low weight and shatter resistance, serious issues are aroused regarding their disposal [1].

The United States Environmental Protection Agency (EPA) estimates that plastics constitute 7.3% by weight (15 - 18% by volume) of the municipal solid waste disposed in U.S. landfills. The EPA also estimates, the quantity of plastic waste will increase by 3% annually between 1986 to 2000. At present, 80% of the solid waste in the United States is landfilled [1].

Landfill is not a good solution for plastic wastes, because that plastic polymers are inert and not degradable. There is also a limited amount of available landfill space. In 1979, there were more than 18,000 landfills in the U.S. That number has declined to about 9,300 in 1986. The landfill sites are closed for various reasons, including the simple fact that they are filled to capacity [2]. Plastic waste from ocean dumping, sewage overflows, and litter have also become a serious environmental problem. Incineration is not a good solution for plastics because their emissions contribute to air pollution.

Recycling seems to be one way to deal with the plastics wastes. Industrial, State and local governments are making numerous and varied efforts on plastics recycling, although at the time of this study, only 10% of the municipal solid waste is being recycled [1]. Most plastic recycling efforts have focused on PET soft drink bottles and to a lesser extent on high-density polyethylene (PE) milk jugs. While approximately 20% of all PET soft drink bottles are recycled, only about 1% of all post-consumer plastic waste is currently recycled [1].

In preliminary studies using melt blown processing lines at the University of Tennessee, Knoxville (UTK), two consumer-waste PET, one industrial-waste copolyester, and a virgin PET were melt blown [3]. Similar basis weight virgin and recycled polymer webs exhibited similar tenacity and bursting strength. The recycled PET webs were uniform in weight and appearance, and had a soft handle with good mechanical properties.

Previous research work at the UTK, using the 20-inch pilot line, demonstrated that recycled consumer-waste polyester (PET) can be processed into usable melt blown webs. Compared with virgin PET, which were tailor made to have a relatively low intrinsic viscosity for melt blown processing, the recycled polymer had a higher I.V., which may have been largely responsible for the larger average fiber diameters, larger pore size and higher air permeability values obtained [4].

The objectives of this study were to understand and improve the melt blowing technology for recycled polyester and to determine the performance properties of the melt blown nonwoven webs produced. In

order to improve the melt blown processing of the recycled PET, attempts were made to decrease the viscosity of recycled PET during processing. Three methods have been investigated: (1) hydrolytic degradation; (2) blending with other polymers; and (3) thermal degradation.

Generally PET polymer must be intensively dried before it is processed. The hydrolytic degradation will take place if there is some moisture with the polymer during processing [5]. However, the degradation to a certain extent may help in decreasing the I.V. of recycled PET and thus improving its processing. Undried PET and dried PET were melt blown at the same processing conditions and the webs produced were evaluated.

Blending is a straightforward and inexpensive method to modify the properties of polymers. Low I.V. virgin PET was used to blend with recycled PET to decrease the viscosity during processing. Significant improvement in properties of PET fibers can be achieved by blending with poly(butylene terephthalate) (PBT) [6-9]. Blending with PBT helps in decreasing the apparent viscosity of PET. Since PBT has similar molecular structure as PET, PBT and PET are compatible. Two grades of PBT were used to blend with recycled PET. One of them had an intrinsic viscosity of 0.88, and the other had a relatively lower I.V. of 0.77. These polymer blends were processed under similar conditions and the webs produced were evaluated.

Since these recycled PET melt blown webs might be used in a high temperature condition, the thermal shrinkage of these webs is very important. The webs, as produced, had shrinkage values as high as 40% at

100 °C. Heat setting is an effective way to control the shrinkage of thermoplastic fabrics. The effects of heat setting on the properties of melt blown webs were studied by evaluating and comparing the web properties before and after heat setting.

CHAPTER II

LITERATURE REVIEW

MELT BLOWN PROCESSING:

Conceptually, the melt-blowing process is old, going back to the 1800s when microfibers of mineral or slag wool were manufactured by extruding the molten slag through bushing and attenuating with high pressure steam jets. In the 1950s, the concept was used to produce polymeric microfibers for possible use in filters. Further research in the 1960s and 1970s demonstrated the commercial viability of the process to produce polymeric microfibers from a wide variety of polymers, asphalts, and polymer blends [10].

The melt-blown web sector of the nonwovens industry is the fastest growing area [10]. In the United States, the annual increase is about 10%, with roll goods sales exceeding $2 billion. Today, there are over 50 commercial installations worldwide [11]. It was also reported that the amount of melt blown materials produced worldwide increased from less than 20 million pounds in 1980 to 46 million pounds in 1984. By the end of 1990, the world market for all melt blown products has been estimated at approximately 100 million pounds, of which 19-20 million (19%) are produced into webs for dry and liquid filtration [11].

Figure I shows a schematic of the basic process of melt blown processing. High-velocity hot air is used to attenuate molten polymer into

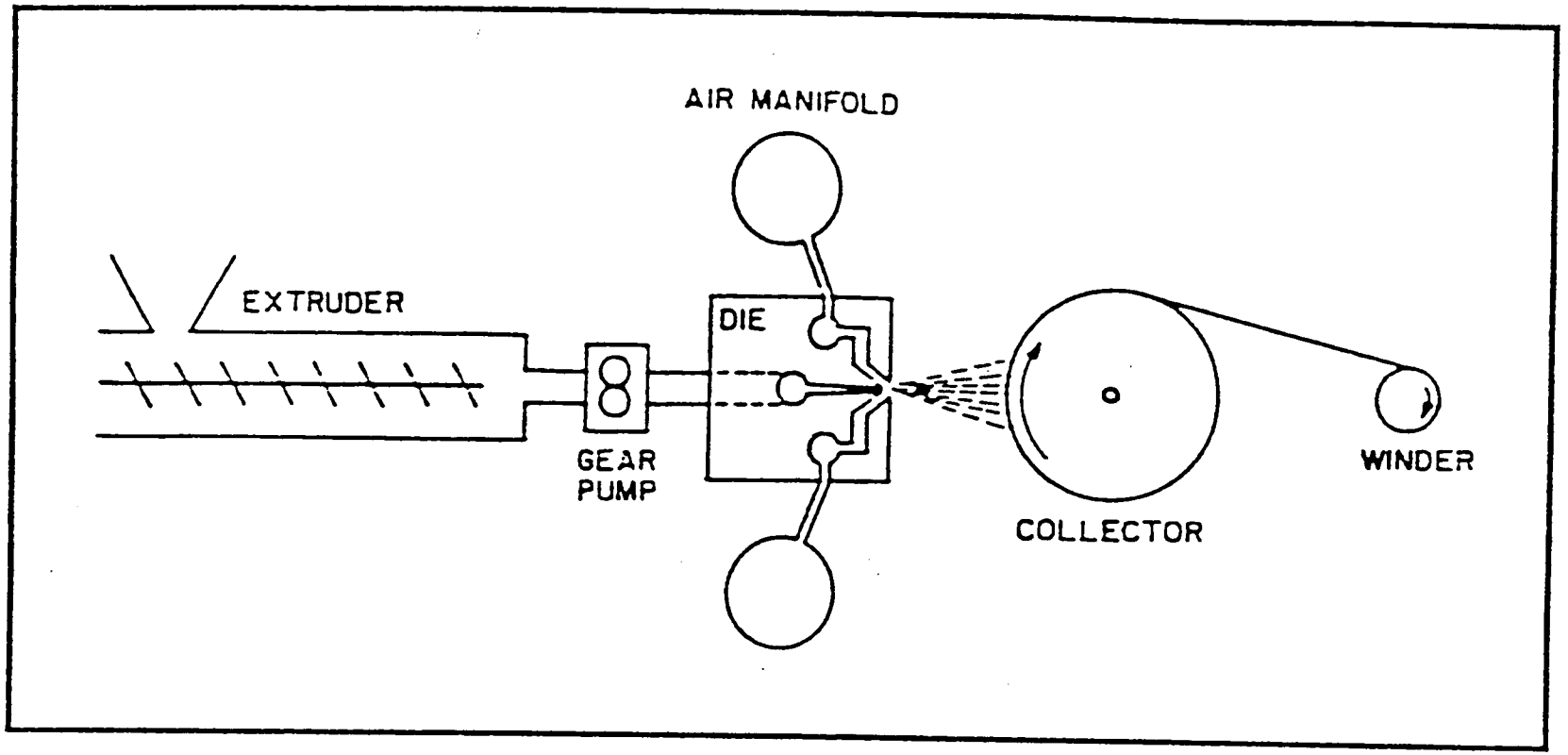


FIGURE I. MELT BLOWING PILOT LINE AT THE UNIVERSITY OF TENNESSEE

very fine fibers. Resin is fed into an extruder where it is melted and heated to the appropriate temperature required for fiber formation. The extruder feeds a special melt-blowing die which is a key to the successful operation of the process. As the resin emerges from the die orifices, it is attenuated by hot high-velocity air, which draws the polymer down into fine fibers. The fibers entangle in the turbulent air steam and then are deposited on the collector screen as a continuous web of entangled fibers. Web integrity is due primarily to fiber entanglement and surface attraction between the very small fibers [12].

The melt blowing process has two categories of process variables: (1) operational variables and (2) off-line variables. The on-line variables include polymer and its throughput, polymer/die and air temperatures, die-to-collector distance, and quench environment. The off-line processing variables include hole size, die set-back, air gap, air angle, web collection type, and polymer/air distribution [13].

One of the real advantages of melt blown processing is its ability to handle many different polymers as well as mixtures of polymers. The polymers which can be melt-blown are listed below. However, the list is not complete.

1. Polypropylene is easy to process and makes good webs.
2. Polyethylene is more difficult to blow into fine fibered webs than polypropylene.
3. Nylon 6 is easy to process and makes good webs.
4. Nylon 11 blows well into an adhesive web that has a very unusual, leatherlike feel.

5. Polycarbonate produces very soft, fine-fibered webs.
6. Polyethylene terephthalate processes easily and gives very soft, fine-fibered webs.
7. Poly(4-methyl pentene-1) blows well into very fluffy, soft webs.
8. Polystyrene produces an extremely soft, fluffy material with essentially no shot [12].

Because of the small fiber diameter, the covering power of even very light-weight sheets is excellent. The webs are normally very soft and drapeable. The web also has some other general properties: enhanced filtration efficiency, good barrier properties, wicking action, softness, and drapeability [12].

Melt blown webs have extremely fine filament diameter of the synthetic fibers and have extremely high specific surface. They can be made with extremely high permeability for a given retention and calendered to yield membrane-like filtration properties. In polypropylene, they are excellent for removing oil from water because of their oleophilic properties and high specific surface. They are used as face mask, micron rated liquid bags, segments of coolant filtration and applications for vacuum cleaners, etc. Of the $818 million total filtration market worldwide, approximately $108 million are melt blown webs [14-16]. Because polyester is acceptable for food contact and melt blown polyester has good strength, a melt blown polyester filter medium is used in the food processing as prefiltration and substitute for membranes [17]. The possible applications of melt blown webs also include: use in battery separators and electrical insulation, wiping cloths, disposable linens, hospital-sanitary pro-

ducts, padding-filling materials, decorative specialties, synthetic papers, synthetic leather bases, adhesive webs, fusible interlines, and agricultural mulches [12].

Melt blowing brings a simple one-step process for converting polymer directly into a nonwoven fabric and is ideally suited for recycling plastics because the process uses hot air to draw the fibers and does not require precise, individual control of each filament as do the conventional fiber spinning processes [10].

In 1984, Exxon Chemical Company installed a 20-inch (50.8-cm) melt blowing pilot line in the Textile Processing Laboratory at UTK and has continued to upgrade the equipment each year to improve the ease of transferring processing parameters to wider production lines. A 6-inch wide (15.24 cm) melt blowing pilot line was also installed at UTK, specially designed with high pressure tolerances for processing high performance polymers and mixed industrial and consumer waste plastics. A 1.25-inch (3.18 cm) screw extruder with four heating zones in the barrel, an adapter, and a two position automatic screen changer were utilized. In order to simplify disassembling and cleaning of the system, a metering pump was not incorporated between the screen changer and the die. The 6-inch line is used to determine the possibility of processing recycled plastics and to develop preliminary processing parameters for trials of polymers on the 20-inch die [4]. A great amount of research on the melt blown process has been done at UTK [19-23].

PLASTICS RECYCLING:

As the plastic industry has grown, the role of plastics in municipal solid waste has become more obvious and worrisome. The annual production of plastics in the U.S. has increased from 3 billion pounds in 1958 to 57 billion pounds in 1988 -- an annual average growth rate of 10.3%. Plastics have many advantages over traditional materials such as wood and glass. Plastics exhibit high resistance to corrosion, low weight, and shatter resistance as well as providing exceptional design flexibility to manufacturers. In addition, plastics are well suited to changing U.S. lifestyles with their increased requirements for convenience and speed, especially in the area of food preparation. Though hundreds of resins have been created for specialty purposes, five resins account for nearly 60% of all U.S. plastics consumption: low-density polyethylene (LDPE), polyvinyl chloride (PVC), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) [1].

Plastic waste accounts for a large and growing portion of the municipal solid waste stream. While contributing only 7% by weight to municipal solid waste stream (**Figure II**), plastics make up an estimated 15 -21% of the volume. Only 10% of the municipal solid waste in the United States is being recycled (**Figure III**). Most post-consumer plastic waste, like municipal solid waste in general, is landfilled. Only about 1% of plastic is recycled [1]. Available landfill capacity is rapidly shrinking. Many sites in the U.S. have been closed for various reasons, including the simple fact that they are filled to capacity. In 1979, there were more than 18,000 landfills for solid waste in the U.S., but that number has declined to

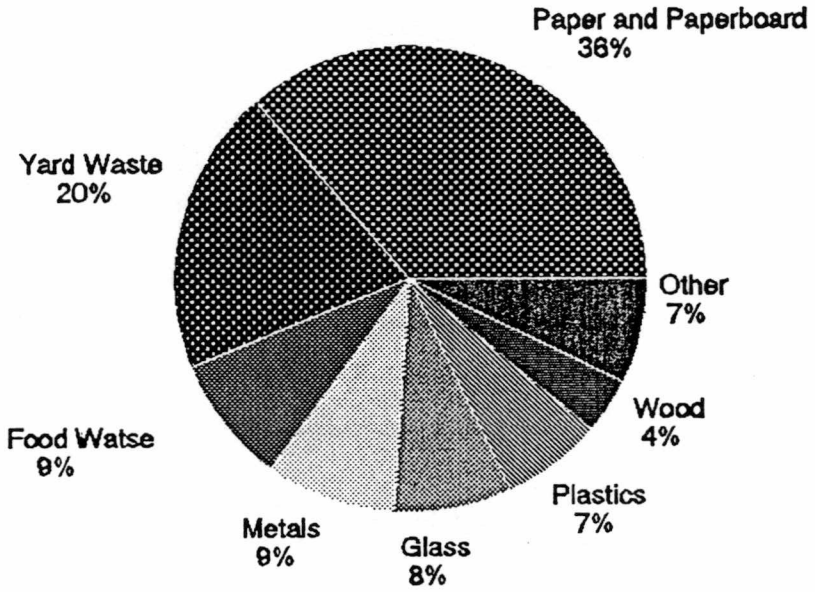


FIGURE II. COMPOSITION OF MUNICIPAL SOLID WASTE IN THE UNITED STATES IN 1986

Source: "Report to Congress, Methods to Manage and Control Plastic Wastes"
United States Environmental Protection Agency.

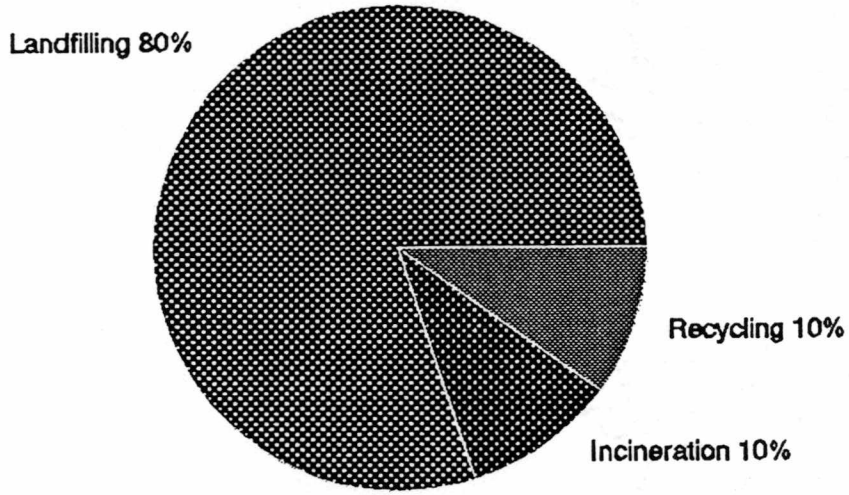


FIGURE III. DECOMPOSITION OF MUNICIPAL SOLID WASTE IN THE UNITED STATES

Source: "Report to Congress, Methods to Manage and Control Plastic Wastes"
United States Environmental Protection Agency.

9,300 in 1986. It is predicted that in the next five to seven years, almost half of the municipal solid waste landfills will reach capacity. Many more are expected to close for reasons such as increasingly stringent regulations on their operations, and few new landfills will be sited [1-2].

Post-consumer waste, is usually destined for disposal and, because these are often in the form of final products or composites, they present the greatest challenge for separation and preparation for recycling. Typical post-consumer plastic waste occur in mixed municipal waste, source-separated items such as plastic beverage containers, used agricultural mulch, or scrapping of major items such as obsolete automobiles [24]. By the nature of polymer manufacture, the base resins are often quite clean. The compounding of these resins to plastics for manufacture is well controlled so that the properties of the products for fabrication are usually narrowly controlled and tailored for a specific use or fabrication technique. When plastics are separated from a mixture of materials, especially if they are separated as a mixture of different kinds of plastics, the final properties must be predictable within a consistent and useful range [25].

Plastic beverage bottles are generally made from poly(ethylene terephthalate) (PET) and sometimes with a base of medium density poly-ethylene. The recycled PET is not likely to be suitable for recycled into a food or beverage container due to health risk of possible contamination Some of the recovered PET is used for molding objects, some for making

fibers for carpet, fiberfill and some in forming new thermosetting plastics. The largest use for recycled PET is fiber spinning for use as fiberfill batting, i.e., as an interliner in clothing or for upholstery [25].

The Melt Blown Processing of Recycled PET:

Previous research work utilizing the 20-inch Exxon melt blown pilot line at UTK [5] demonstrated that recycled consumer-waste polyester (PET) can be processed into usable melt blown webs. Compared with the virgin PET used, which were tailor made to have a relatively low intrinsic viscosity of 0.59 for melt processing, the recycled polymer had a higher I.V. of 0.62. The high I.V. may have been largely responsible for the larger average fiber diameters, larger pore size and higher air permeability values that were obtained. There was also an indication of a potential problem with screen clogging during melt blowing of the recycled PET. The screen contained a substantial amount of carbonized residue after the recycled PET melt blow trials.

In preliminary studies [4] using the 2.5-inch melt blown die at UTK, two consumer-waste recycled PET polymers, one industrial-waste copolyester, and a virgin PET were melt blown. The virgin and recycled polymer webs of the same basis weights exhibited similar tenacity and bursting strength at corresponding air flow rates. Recycled PET webs exhibited better dimensional stability at higher temperature. The recycled PET webs were uniform in weight and appearance, and had a soft tactile handle with good mechanical properties.

Thermal and Hydrolytic Degradation:

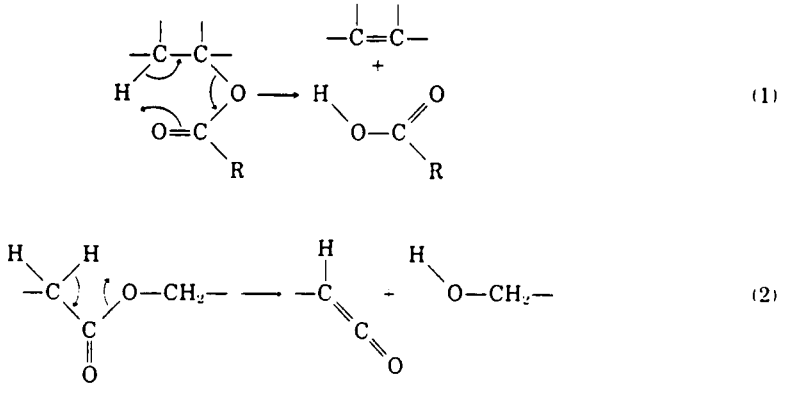
Degradation is generally looked upon as an undesirable process. However, degradation may not always be viewed as harmful, as may be seen in the mastication of rubber, where mechanical force, such as shearing, is employed to lower its molecular weight to such levels as to render the rubber processible and commercially useful.

Broadly, degradation of polymers may be considered as any type of modification of a polymer chain involving the main-chain backbone or side groups or both. The degradative process which affects the breaking of primary valence bonds, essentially in the chain backbone, with a concomitant decrease in the polymer molecular weight, may be achieved by the following types of degradations: (a) thermal ; (b) hydrolysis (oxidative); (c) radiative; (d) mechanical; (e) chemical; (f) biological [26]. The main chain breakage in polymer degradation will result in decrease of molecular weight of the polymer. Positive coefficiency was found between molecular weight, intrinsic viscosity and melt viscosity for PET and PBT [33-36].

A considerable amount of research has been done on the degradation of polyesters [27-32]. Polyesters are heterochain macromolecular substances characterized by the presence of carboxylate ester groups in the repeating units of their main chains.

The thermal stability of linear aliphatic polyesters is generally excellent up to 200 ^{o}C. In the range of 200 - 250 ^{o}C, particularly in vacuum and in the presence of catalysts, these and many other types of poly

-esters undergo depolymerization to cyclic mono-, bi, or higher esters or lactones. At higher temperatures (> 250 ^{o}C), more general decomposition ensues, typically with the formation of vinyl and carboxyl groups by ester scission by a cyclic elimination mechanism (**Equation. 1**); four-center cleavage to ketene groups (**Equation. 2**) has also been proposed [27-28].



(1)

(2)

(1) Formation of Vinyl and Carboxyl Group By Ester Scission By a Cyclic Elimination Machinism
(2) Four-center Cleavage to Ketene Groups

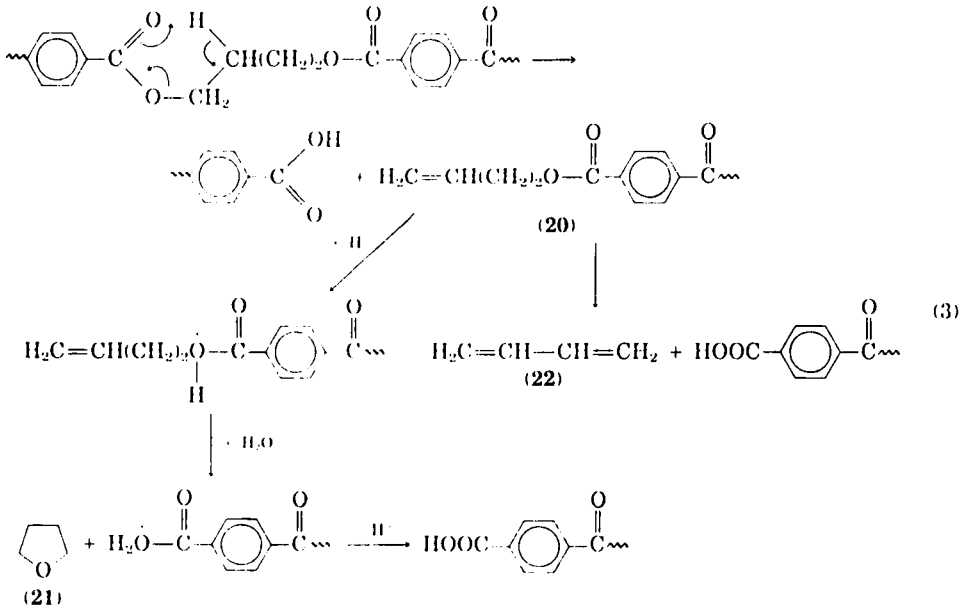
PET and PBT are prone to attack by oxidizing reagents and particularly by aqueous alkalis, which etch them away by hydrolysis proceeding from the surface, and ammonia and lower amines, which can permeate into the interior, causing degradation by aminolytic cleavage of the ester groups [28].

Although each polyester will have its own detailed mechanism and volatile products of degradation, there is a good deal of common ground between them. For example, the major initial step in all cases where Beta

hydrogen atoms are available is invariably alkyl-oxygen scission involving a six-membered ring transiton state, which in poly(ethylene terephthalate) is reflected in the formation of vinyl and carboxyl end groups [31-32].

Because of low moisture absorbency, polyesters are essentially unaffected by water at ordinary temperatures, but at higher temperatures water or humid atmospheres hydrolyze the ester groups to -OH and -COOH, the latter being autocatalytic leading to further hydrolysis. Since hydrolysis by water occurs rapidly at temperatures above 150 ^{o}C, PET and PBT must be dried intensively to reduce moisture contents to less than 30 ppm before processing from the melt [28].

At high temperatures, eg. during the relatively long time periods involved in melt processing, PET and PBT undergo thermal degradation, inherently by Beta-scission reaction of **Equation 1**. Proposed mechanisms for the thermal degradation of PBT and PET are shown in **Equation 3** and **4**, respectively [28].



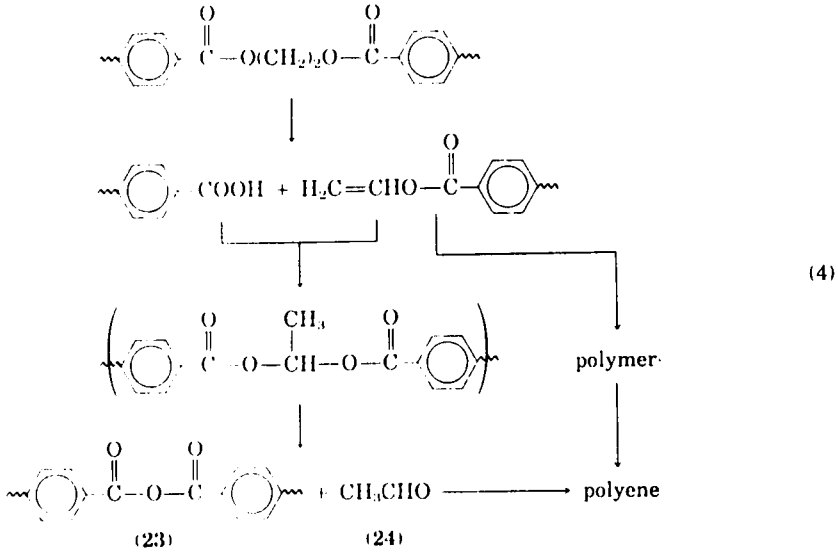
(3)

Thermal Degradation of PBT:

(20) Transformation of the 3-butenyloxycarbonyl-phenylene Fission Fragment

(21) An Ionic Path by Protonation Forms Tetrahydrofuran

(22) A Car boxyl End Group; A Second Concerted Ester Pyrolysis Reaction Yields Carboxyl; 1,3-butadiene



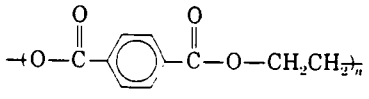
(4)

Thermal Degradation of PET:

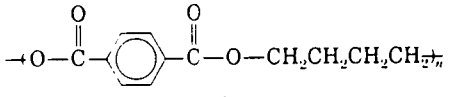
The Primar Scission leads to Carboxyl and Vinyl Easter Intermediate Forming Carboxylic Anhydride Linkage Plus Acetaldephde

Poly(ethylene terephthalate) and Poly(butylene terephthalate):

By definition, polyester is a polymer composed of at least 85 wt% of an ester of dihydric alcohol (HO-R-OH) and teraphthalic acid (p-HOOC-C_6H_4-COOH). The most widely used polyester in textile application is linear PET. PBT is another type of polyester. A great amount of research has been done on crystalline structure and rheological properties of PET and PBT [37-40]. The molecular formulas of PET and PBT are shown below. PET (1); PBT (2).



(1)



(2)

Blending provides a straightforward, versatile and relatively inexpensive method to develop new polymeric materials with superior combination of useful properties. Blends of various polymers were studied in previous research [41-50]. Several researchers have studied the blending of PET and PBT polymers in processing [6-9]. Different thermodynamic concepts, i.e., heat of mixing approach, interaction parameter approach and free energy approach, were applied to predict the compatibility of PET and PBT blends. The results predict that the system behaves as a compatible polymer pair and can serve as a good guide to solve practical problems [9].

Recent studies [7-9] indicated that significant improvement in properties of PET fiber can be achieved by blending with PBT. PET and PBT blends are predicted to be compatible in the amorphous state. However, they crystalize separately according to their own unit cell structure. Due to their peculiar characteristics, they are expected to produce fibers having significantly different properties at different proportions and processing conditions.

The previous study showed: PET and PBT had different modulus values due to structural differences. The modulus values of the blends were within the limits of the values proposed by Nielson. A blend containing 98/2, PET/PBT showed a higher modulus and strength value due to high intercrystalline links. Blends containing 10% PBT probably had a fine grain structure, which on drawing produced an interconnected structure with high density of tie molecules, resulting in high modulus and comparatively high strength [7].

The polymer alloy fiber prepared from PET and 0-10% PBT by sequential melt-blending and spinning showed a single glass transition temperature, which was lower than that of 100% PET. The melting point of the blended fibers was lower than that of 100% PET owing to the decrease in crystalline order and partial transesterification [7].

The flow behaviors of linear polyethylene, poly(butylene terephthalate) and poly(ethylene terephthalate) were studied. The viscous and elastic properties were investigated using an Instron Capillary Rheometer and the Philippoff-Gaskins-Bagley analysis. The order of decreasing viscosity is HDPE > PET > PBT; the order of decreasing acti-

vation energy is PBT > PET > HDPE.

The activation energies decreased with increasing shear rate and with decreasing die entry angle. The activation energy was related to the sensitivity of the melt viscosity to changes in temperature. The larger the activation energy, the more sensitive the polymer to changes in temperature. Although PBT is more flexible than PET and is expected therefore, to have a greater entanglement density, the ranking of the expected order is reversed. It was suggested that the reversal of the expected order was due either to increased polar interaction in PET due to a great number of terephthalate acid moieties in polymer chain, or to increased plasticization in PBT due to oligomer content [8].

The rheological behaviors of PET and PBT blends were studied by Mishra and Deopura [6]. The results indicated that the blending of two materials provides a means of improving the physical properties of polymers, and at a certain blending ratio, the melt viscosity of the blend reaches a minimum.

The addition of small amount of PBT (up to about 3%) to PET produces an increase in viscosity and decrease in activation energy, which may be associated with a higher entanglement density. For more than 4% of PBT, there is a decrease in the viscosity and an increase in activation energy, which may be due to parallel phase segregation [6].

CHAPTER III

PROCEDURE

The purpose of this study was to investigate three methods to improve melt blown processing of recycled PET and the effect of heat setting on the melt blown webs. The research was conducted as follows:

1. The polymers were prepared for melt blown processing. Dried and undried PET and blends of different polymers in different ratios were prepared according to the description in the following sections.

2. The prepared polymers were processed on the melt blowing lines at UTK. The comparison web pairs were processed under similar processing conditions. Higher die temperature and heating zone temperatures were used to investigate the effects of higher processing temperature.

3. The webs were heat set in a constant temperature oven under three different conditions.

4. The properties (i.e., mechanical properties, fiber diameter, air permeability, filtration efficiency, shrinkage, etc.) of the webs were evaluated.

Materials

All the materials used in the study are listed in **Table I.**

TABLE I.

THE POLYMERS USED IN THIS STUDY

Polymers	Form	Source	I.V. (dl/g)
Recycled PET	Flake	Far Eastern Textile Limited.	0.83
Recycled PET	Flake	Day Products Company.	0.83
High I.V. PBT	Pellet	BASF Corp.	0.88
Low I.V. PBT	Pellet	BASF Corp.	0.77
Virgin PET	Pellet	Eastman Chemical Products, Inc.	0.62

Processing

Melt blowing trials for this study were performed on the 6-inch wide melt blowing pilot line, which was especially designed with high pressure tolerance for processing recycled plastics. A 1.25-inch screw extruder with four heating zones in the barrel, an adapter, and a two position manual screen changer were utilized. The detailed line conditions used for different polymers are given in **Tables II** and **III**. In all these trials, efforts were made to adjust the collector speed to achieve web basis weights of 25 to 50 g/m^2 (0.75 and 1.5 oz/yd^2, respectively).

TABLE II.

PROCESSING CONDITIONS USED IN MELT BLOWING

Samples	Screw Speed (rpm)	Melt Pressure (psi)	Die Temperature (°C)	Air Flow Rate (Valve (Opening %)
1A, 2A	35	1200	289	35
1B, 2B	22	400	289	45
3A, 3B	35	800	282	35
4A, 4B	35	850	289	35
5B, 5C	25	400	315	45

* The Die-Collector-Distance was 17.8 cm for all trials.

1A : Dried Recycled PET (Day Products Co.)

2A : Undried Recycled PET (Day Products Co.)

1B: Dried Recycled PET (Far Eastern Textiles Ltd.)

2B: Undried Recycled PET (Far Eastern Textiles Ltd.)

3A: 80% Recycled PET/ 20% High I.V. PBT

3B: 80% Recycled PET/ 20% Low I.V. PBT

4A: 75% Recycled PET/ 25% Low I.V. PET

4B: 50% Recycled PET/ 50% Low I.V. PET

5B: Recycled PET Processed at Increased Die Temperature

5C: Recycled PET Processed at Increased Heating Zone and Die Temperatures

TABLE III.

PROCESSING CONDITIONS FOR RECYCLED PET
(HIGH TEMPERATURE PROCESSING)

Sample	Barrel Zone#1 (°C)	Barrel Zone#2 (°C)	Barrel Zone#3 (°C)	Adapter Zone (°C)	Die Temperature (°C)
Others	232	271	287	287	289
5B	232	271	287	287	315
5C	232	279	304	304	315

Others: 1A, 2A, 1B, 2B, 3A, 3B, 4A, 4B (as described in Table II)

5B: Recycled PET Webs Produced at Increased Die Temperature

5C: Recycled PET Webs Produced at Increased Heating Zone and Die Temperature

Dried PET vs Undried PET. To investigate the effect of moisture in the recycled PET, two trials were performed, using recycled PET flakes from Day Products Co. and Far Eastern Textile Ltd.. The "dried PET" was prepared by heating the recycled PET flakes in a constant temperature oven (Model: DK-63, Scientific Products, Japan) at 160 ^{o}C for four hours (however, the air was not pre-dried) and then storing it in air-tight bottles until processing. The "undried PET" was heated at the same conditions as the dried PET and then, exposed to standard atomospheric conditions (20 - 25 ^{o}C; 60 - 80% r.h.) for at least 24 hours to allow it to regain moisture. Heating was done to achieve crystallization. The moisture content of the undried Day Products PET was 0.111%, tested by weighing the polymers before and after drying in a microbalance. Moisture content of the undried and dried Far Eastern PET polymer were 0.263% and 0.00713% respectively, determined using a moisture analyzer (model: CA-06, Mitsubishi Instruments, Japan). The comparison web pairs produced from dried and undried PET were processed under similar conditions (**Table II**).

Polymer Blending. PBT, a polyester with a melting temperature (T_m: about 220 ^{o}C) lower than that of PET and low molecular weight PET, were blended with recycled PET. Recycled PET from Far Eastern Textile Ltd. was blended with two grades of PBT from BASF Corp. and a virgin low I.V. PET from Eastman Chemical Products, Inc. as follows:

-- 80% Recycled PET/ 20% High I.V. PBT

-- 80% Recycled PET/ 20% Low I.V. PBT

-- 75% Recycled PET/ 25% virgin PET

-- 50% Recycled PET/ 50% virgin PET

The PBT and low I.V. PET were virgin polymers because recycled materials in those grades could not be obtained at the time of this study. These blends were prepared by weighing the predried polymers and hand mixing. The mixtures were fed directly into the extruder. Processing conditions are listed in **Table II.**

Processing at Higher Temperature. Two different approaches were used to increase the processing temperature. In the first case, die temperature was increased from 290 to 315 °C. In the second case, the temperature of heating zones in the barrel were gradually increased in addition to increasing the die temperature from 290 to 315°C. All the other processing conditions were unchanged (**Table III**).

Heat Setting. In order to control the thermal shrinkage of the melt blown webs, the effects of heat setting on the properties of the melt blown webs were studied. The webs (L= 10", W= 6") were fixed on a cardboard frame by spring clips as shown in **Figure IV**. The area of the web used for testing was taken from the central part of the web (L= 8", W= 4"). A constant temperature oven (Model: DK-63, Scientific Products, Japan) was used for the heat setting experiments. Three heat setting conditions were used:

-- 125 °C, 3 minutes

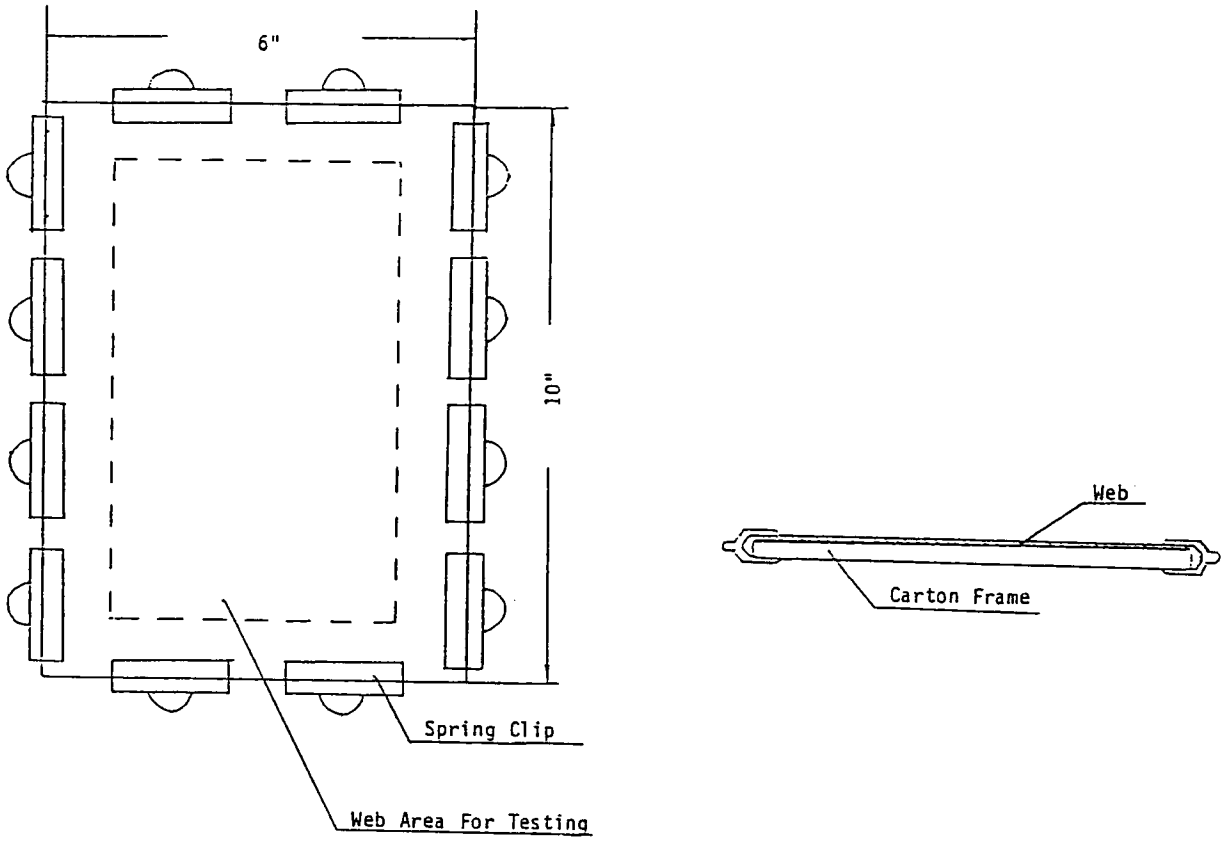


FIGURE IV. THE HEAT SETTING OF MELT BLOWN WEBS

-- 150 °C, 3 minutes

-- 150 °C, 5 minutes

The cardboard frame with the samples mounted were inserted in the oven at the preset temperatures. After heating for preset time, they were removed and characterized.

Determination of Web Properties

Physical properties of the melt blown webs evaluated. The tests which were performed are listed in **Table IV**, with their corresponding ASTM methods. Tests methods which do not have a corresponding ASTM method are described below.

Tenacity and Elongation-to-break. Tensile testing was done using the Instron tensile tester (Model TM, Instron Corp., Carton, Mass.). Because all the melt blown webs in this study were processed on the six-inch melt blown line, it was difficult to use 4" gauge length, recommended by ASTM D 1682-64, especially when testing the webs in the cross direction. The sample size was 4" x 1" and the gauge length was two inches. The cross head speed used was 5 inches/min. The data reported is an average of five samples in each case.

Fiber Diameter. The diameter of the fibers in the webs were measured using an ETEC Auto-scan scanning electronic microscope (Hayward, CA). The sample webs were sputter coated for one and three quarter minutes with gold using a Technics Hummer II (Alexandria, VA).

TABLE IV

TEST METHODS FOR PHYSICAL PROPERTIES OF MELT BLOWN WEBS

Property Measured	Standard Method
Basis Weight	ASTM D 3776-85
Thickness	ASTM D 1777-64
Air Permeability	ASTM D 737-75
Bursting Strength	ASTM D 3787-80A
Stiffness	ASTM D 1388-64
Pore Size	ASTM F 316-86
Tenacity and Elongation-to-break	_____
Fiber Diameter	_____
Filtration Efficiency	_____
Intrinsic Viscosity	_____
Thermal Shrinkage	_____
Differential Scanning Calorimetry (DSC)	_____
Rheological Properties	_____

The temperature rise during sputter coating was less than 10°C/min. Colloidal graphite paint was used to ground the edges of the web to the stud to reduce charging. Five photomicrographs were taken for each web. The magnifications used ranged from 300 to 600 times. Two diagonal lines were drawn across each photomicrograph and the diameters of all the fibers at the points the line crossed were measured. The reported fiber diameter values represent a average of fifty such measurements.

Filtration Efficiency. The filtration efficiency was determined using nebulized water emulsion of polystyrene microspheres. The flow rate of dried, micro-filtered air to the nebulizer and the delusion air flow rate were maintained at 3.5 and 61.4 liters per minute, respectively. A Hiac/Royco Airborne Particle Counting System consisting of a 4100 Particle Counter and 1200 Sensor were used to determine the filtration efficiencies of webs to both 0.5 and 0.8 micron latex particles, upon exposure to a mixture of the two sizes (1:1 mixture with respect to the numbers of particles). The numbers of latex particles which passed the sample chamber with and without a melt blown sample were used in the following equation to calculate the filtration efficiency [4]:

$$\text{Filtration Efficiency} = \frac{\text{Count without a filter - Count with a filter}}{\text{Count without a filter}}$$

Intrinsic Viscosity. The intrinsic viscosities of polymers and webs were measured, using 60:40 phenol/ tetrachloroethane as the solvent and Cannon-fenske 150 viscometer. The solution concentration used was 0.4975 g/dl. The efflux times for the solvent and solutions were

measured at 30°C. The relative viscosity is equal to ts/to, where ts is the efflux time for the solution and to the efflux time for the solvent. Intrinsic viscosity was calculated from relative viscosity by Solomon-Ciuta equation [51].

$$[\eta] = \frac{\sqrt{2}}{C} \left(\eta_{sp} - \ln\eta_{rel}\right)^{\frac{1}{2}}$$

$[\eta]$: *intrinsic viscosity;*
η_{rel}: *relative viscosity;*
η_{sp}: *specific viscosity* $(\eta_{rel}-1)$;
C : *concentration of solution (g/dl).*

Thermal Shrinkage. The thermal shrinkage of the melt blown webs was measured using a Constant Temperature Oven (Model DK-63, Scientific Products, Japan). The web strips in both machine and cross directions (L= 6", W= 1"), on which two lines were drawn with a separation of four inches, were put in the oven at 100°C for 5 minutes. The distance between these two lines on the web strip were measure after heating and the shrinkage were calculated by the following equation:

$$\text{Shrinkage (\%)} = \frac{\text{Initial Gauge (4")} - \text{Gauge after Heating}}{\text{Initial Gauge (4")}} \times 100$$

Differential Scanning Calorimetry (DSC): The instrument used for calorimetric measurements was a Mettler DSC25 (Mettler Instruments, Treifensee, Switzerland). The samples were scanned at a heating rate of 10 ^{o}C/min, between 50 and 300^{o}C. The sample size used was about 12 mg in all the cases. Nitrogen was used to purge the sample chamber during the scans.

Rheological Properties: The melt viscosity was determined by using an Instron capillary rheometer. The capillary die had an orifice of 0.4 mm diameter and a L/D ration of 10/1. Measurements were made at a temperature of 280^{o}C. Load responses were recorded at crosshead speeds of 0.2, 0.5, 1.0, and 2.0 inches/min. The shear viscosity is the wall shear stress divided by non-Newtonian wall shear rate. The melt viscosity was calculated using the relationship between wall shear rate and shear stress as suggested by C. D. Han [52].

CHAPTER IV

RESULTS AND DISCUSSION

Three methods (using undried PET instead of dried PET, blending recycled PET with other polymers in **Table I**, and two higher processing temperatures described in **Table III**) were investigated as means to improve the quality of melt blown nonwoven recycled PET. The resultant webs were evaluated (**Table IV**). Some of the melt blown webs were heat set under three different conditions (125°C, 3 minutes; 150 °C, 3 minutes; 150 °C 5 minutes). The effect of heat setting was studied by evaluating the properties of the web such as, shrinkage and mechanical properties, before and after heat setting.

Processing Observations

All of the recycled PET processed in this study were in flake form and the PBTs (both high and low I.V.) and low I.V. PET were in the pellet form. The major problem encountered in the processing of flakes was that feeding into the extruder was not uniform. This led to fluctuations in pressure at the die. Because there was no forced feed system to handle high bulk density polymers, the flakes were forced into the extruder by pushing with a mallet. This helped in maintaining continuous feeding of the flakes and web formation.

As long as the pressure was maintained between 350 and 500 psi at the die, uniform shot free webs could be collected. Only those webs which were free of shot and also of uniform basis weight were used for characterization. Since the recycled flakes were clean and were free of any visible contamination, no problems like screen clogging were noticed and the webs produced were white with no indication of any visible degradation.

The Web Properties

Dried PET vs Undried PET. Typically, polyester polymers are dried before extrusion in order to remove the moisture, because the moisture increases hydrolytic degradation during processing. However, it was proposed that with the recycled PET, with higher molecular weight than that of fiber-grade PET, degradation to some extent may be helpful, because lowering the molecular weight makes processing easier and results in finer fibers in the webs.

The properties of the webs produced from dried and undried recycled PET from Day Products Co. and Far Eastern Textile Ltd. are shown in **Table V** and **Table VI**. From the comparison pairs of webs (1A and 2A; 1B and 2B) produced from dried and undried PET with similar basis weight, it was evident that the webs produced from undried PET had lower fiber diameter (**Fig. V**). For the webs of basis weight 0.7 oz/yd^2,which were produced from the Day Products recycled PET, the fiber diameter decreased from 15.0 μm of the dried PET webs to 9.9 μm

TABLE V.

BASIS WEIGHT, THICKNESS, FIBER DIAMETER, AIR PERMEABILITY, SHRINKAGE AND FILTRATION EFFICIENCY OF WEBS PRODUCED FROM DRIED AND UNDRIED PET

Samples	Basis Weight ($oz/yard^2$)	Thickness (μm)	Fiber Diameter (μm)	Air Permeability ($m^3/s/m^2$)	Shrinkage (%) MD	Shrinkage (%) CD	Filtration Efficiency (%)
1A (Dried)	0.67	284.5	15.0	5.21	26.3	3.8	38.7
2A (Undried)	0.74	259.1	9.9	2.78	26.5	17.2	45.0
1B (Dried)	1.15	312.6	13.9	1.38	35.3	11.3	50.5
2B (Undried)	1.28	309.6	9.0	0.98	32.0	11.3	60.6

1A: Dried Recycled PET (Day Products Co.)

2A: Undried Recycled PET (Day Products Co.)

1B: Dried Recycled PET (Far Eastern Textiles Ltd.)

2B: Undried Recycled PET (Far Eastern Textiles Ltd.)

TABLE VI

MECHANICAL PROPERTIES AND INTRINSIC VISCOSITY OF WEBS PRODUCED FROM DRIED AND UNDRIED PET

Samples	Tenacity (mN/tex) MD	CD	Elongation (%) MD	CD	Bursting Strength (kPA)	Stiffness (mg.cm)	Intrinsic Viscosity(dl/g)
1A (Dried)	6.1	3.40	44.0	96.0	21.1	83.0	0.62
2A (Undried)	8.6	5.98	49.5	78.0	25.8	73.0	0.58
1B (Dried)	11.5	4.75	25.0	140.0	33.6	332.0	0.59
2B (Undried)	9.8	6.91	50.0	95.0	34.5	300.0	0.62

1A: Dried Recycled PET (Day Products Co.)

2A: Undried Recycled PET (Day Products Co.)

1B: Dried Recycled PET (Far Eastern Textiles Ltd.)

2B: Undried Recycled PET (Far Eastern Textiles Ltd.)

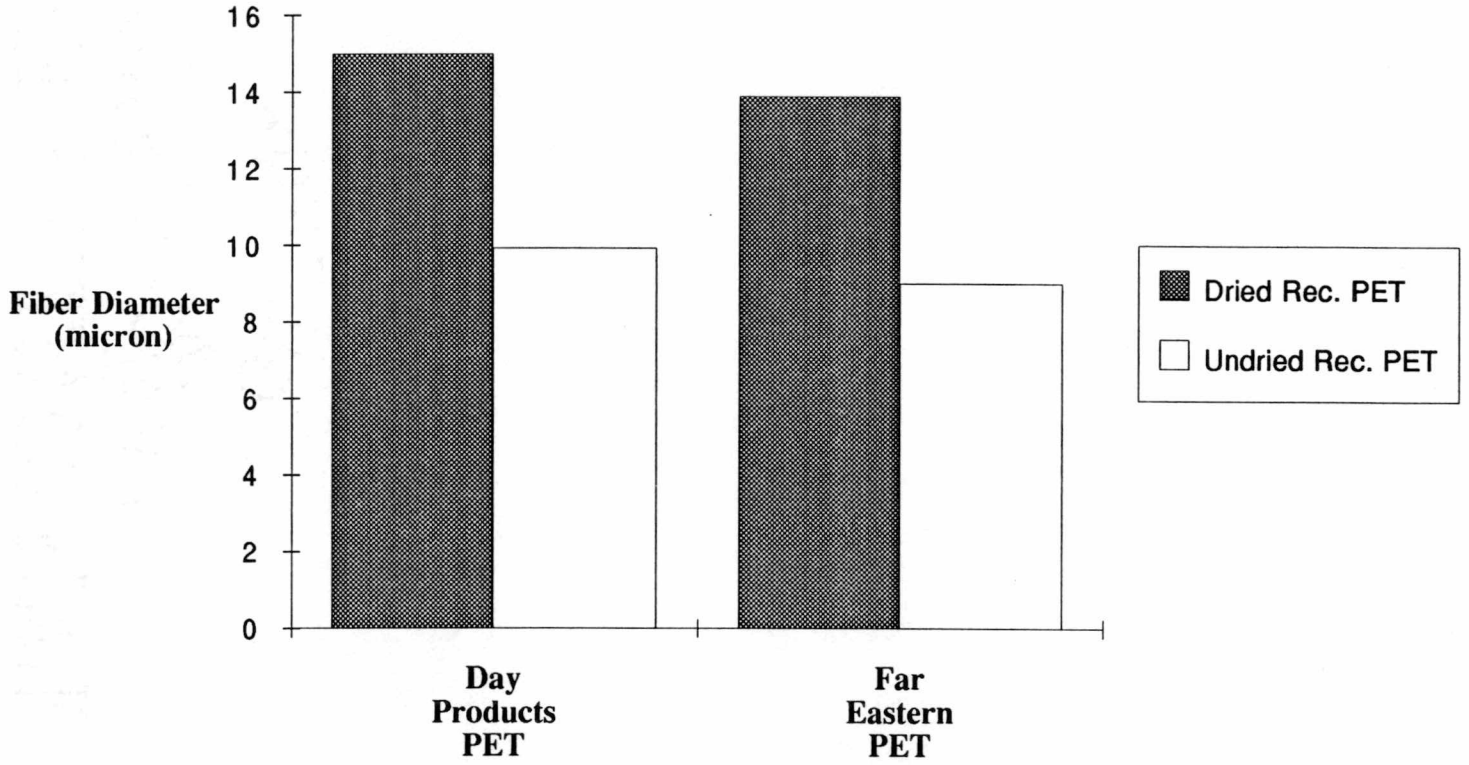


FIGURE V. FIBER DIAMETER OF WEBS PRODUCED FROM DRIED AND UNDRIED RECYCLED PET

for undried PET webs, which is a drop about 30%. Also, for the webs of basis weight 1.3 oz/yd^2, which were made from Far Eastern recycled PET, the fiber diameter decreased from 13.9 μm to 9.0 μm. Although dried and undried PET webs had similar basis weight, the undried PET webs also were thinner, which indicates a more compact packing of fibers in the web. This compact structure of undried PET webs is responsible for the lower air permeability (**Fig. VI**) than that of webs produced from dried PET.

The webs produced from undried PET also showed a higher tenacity in machine direction than the dried PET webs (**Fig. VII**). For the webs of basis weight 0.7 oz/yd^2, the machine direction tenacity increased from 6.1 mN/tex of dried PET webs to 8.6 mN/tex of the undried PET webs, which is an increase of about 40%. Tenacity in the cross direction and bursting strength values were almost the same in these two cases. Breaking elongation data were not consistently different in the two cases. However, during tensile testing, it was observed that the load-elongation curves of these two kinds of webs were different (**Fig. VIII**). The undried PET webs had a higher initial modulus than dried PET webs, which was due to the more compact structure of undried PET webs. The undried PET webs also had a smooth and soft hand, since they had lower stiffness than dried PET webs (**Table VI**).

The webs produced from undried PET (2A, 2B) had lower intrinsic viscosity after processing (**Table VI**). The undried PET degraded more during the melt blowing process than the dried PET.

The comparison pairs of dried and undried PET webs were produc-

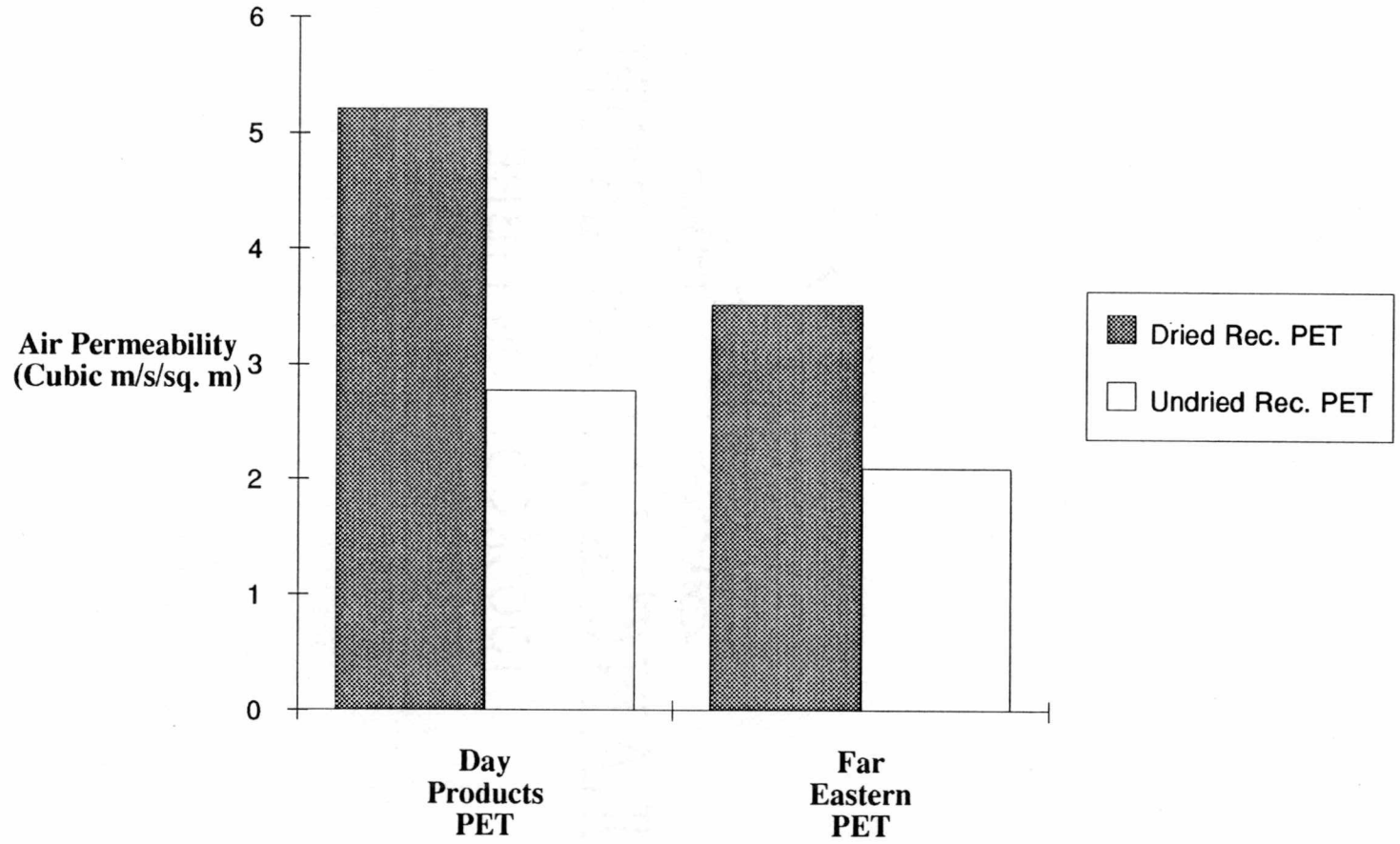


FIGURE VI. THE AIR PERMEABILITY OF WEBS PRODUCED FROM DRIED AND UNDRIED PET

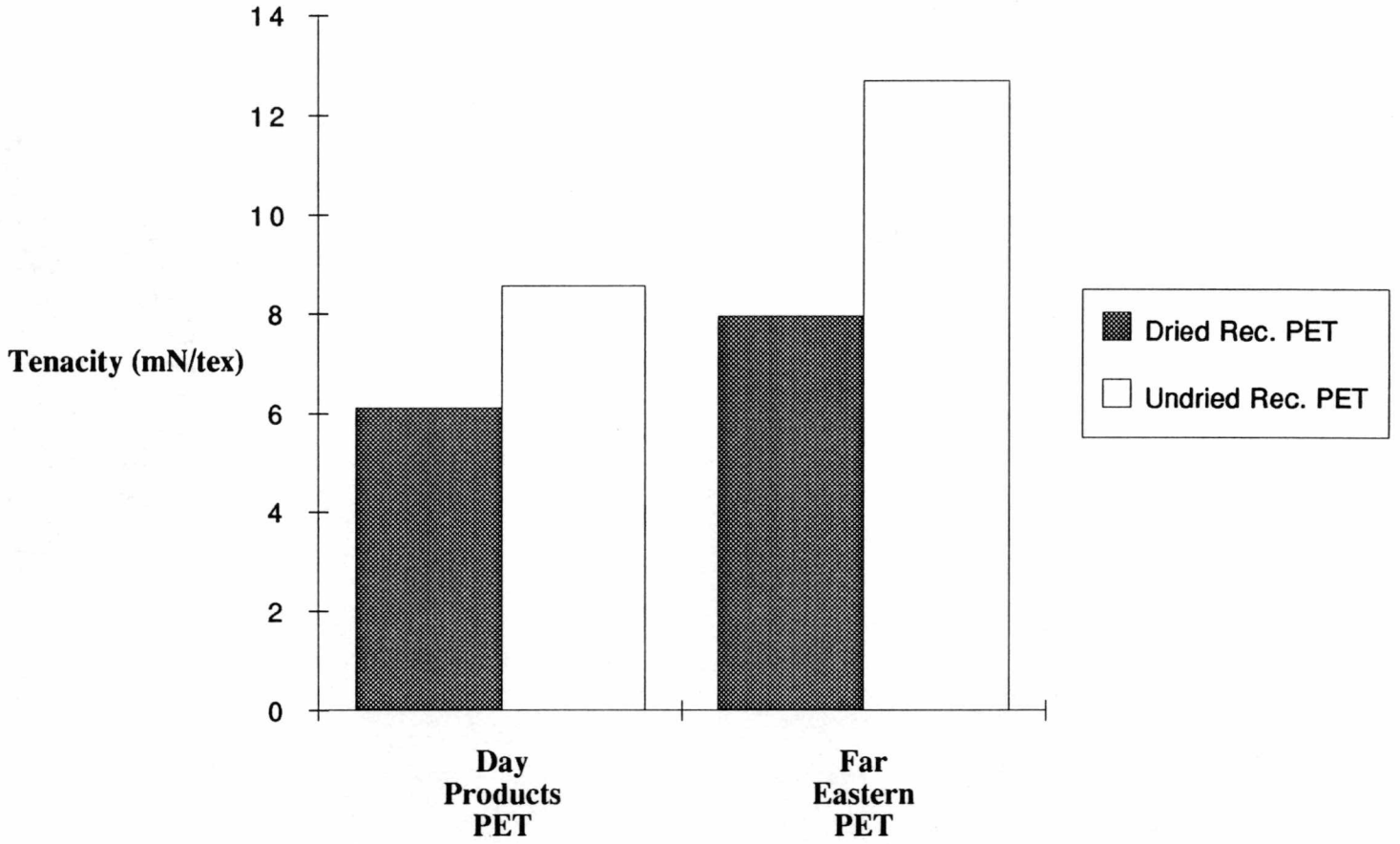


FIGURE VII. THE TENACITY IN MACHINE DIRECTION OF WEBS PRODUCED FROM DRIED AND UNDRIED RECYCLED PET

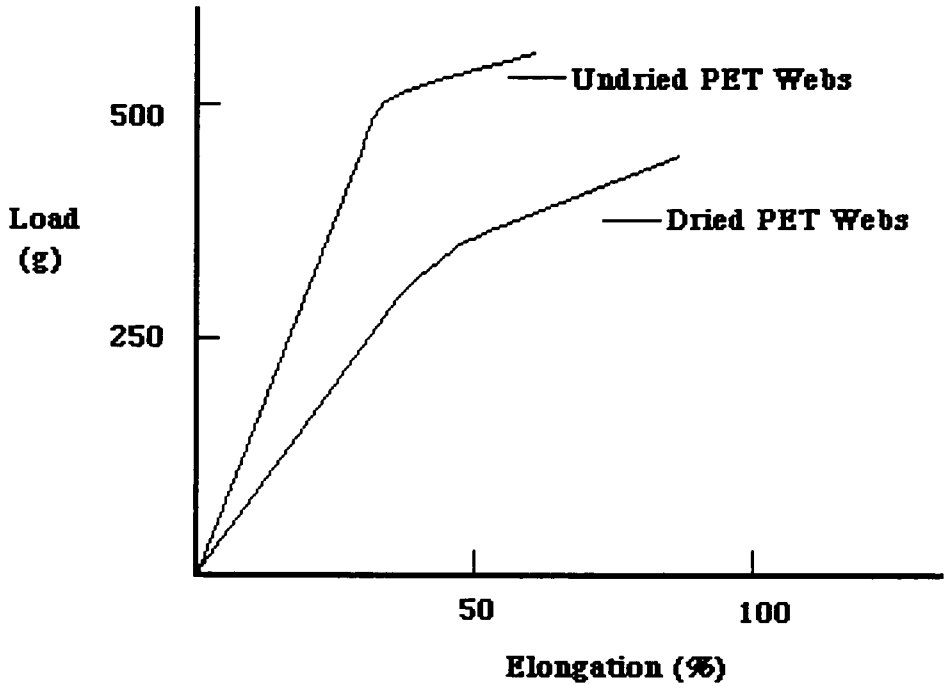


FIGURE VIII. TYPICAL LOAD-ELONGATION CURVES OF DRIED AND UNDRIED PET WEBS

ed from the same source (Day Products Co. or Far Eastern Textiles Ltd.) and were processed under the same conditions. The only difference between the two conditions was their moisture content, i.e., undried PET had more moisture (0.263%, measured by moisture analyzer (model: CA-06, Mitsubishi Instruments, Japan)) than dried PET (0.00713%, measured by the same instrument). The decrease in intrinsic viscosity, which is related to the molecular weight of the polymer, indicated that the undried PET degraded during the process. This degradation was mainly responsible for the improved performance properties of the webs produced from undried PET. The possible mechanisms of such a degradation are reviewed in Chapter II (pages 15 - 19).

From the previous studies [3-4], it is known that lower viscosity of the polymer results in easier processing and smaller fiber diameters, and consequently more compact webs. The comparison pair of these two kinds of webs for testing had similar basis weight, which means the webs with smaller fiber diameter had larger number of fibers in a unit area. Because the undried PET webs were thinner, they had a more compact structure than the dried PET webs. The air permeability of webs, which was measured by testing the air flow through the webs at a pressure drop of 0.5 inches of water, was largely dependent on web structure. The more compact web structure of undried PET webs resulted in lower air permeability.

From **Figure VIII**, it is evident that dried and undried PET webs had different load-elongation curves. The undried PET webs had higher

initial modulus than dried PET webs, which may be due to their more compact web structure and reduced fiber slippage. The figure also shows that the undried PET webs had higher breaking strength. The compact structure of fibers in the web may have contributed to the observed higher tenacity in the machine direction and different load-elongation behaviors.

Blending Recycled PET with Other Polymers. The recycled PET was blended with two grades of PBT (I.V.= 0.88, and I.V. = 0.77) at a ratio of 80/20, and with a low I.V. PET at ratios of 75/25 and 50/50. Blending with PBT and low I.V. PET could lower the melt viscosity during processing thereby improving properties of the recycled PET webs.

The properties of the webs produced from these polymer blends are shown in **Table VII** and **Table VIII**. Although the webs have similar basis weight (0.7 oz/yd^2), the webs produced from recycled PET blended with two grades of PBT had lower intrinsic viscosity (**Fig. IX**). The PET/PBT webs also had smaller fiber diameters (**Fig. X**), had less air permeability (**Fig. XI**) and higher tenacity in machine direction (**Fig. XII**) and were thinner than 100% recycled PET webs. The webs produced from recycled PET blended with low I.V. PBT had more notable property changes than those webs produced from recycled PET blended with high I.V. PBT.

PBT is a polyester with a melting temperature (T_m: about 220°C) lower than that of PET (T_m: 260°C). PBT and PET have similar molecular structure, which makes them compatible. Previous research [7] showed that

TABLE VII.

BASIS WEIGHT, THICKNESS, FIBER DIAMETER, AIR PERMEABILITY, SHRINKAGE AND FILTRATION EFFICIENCY OF WEBS PRODUCED FROM BLENDS OF RECYCLED PET

Samples	Basis Weight ($oz/yard^2$)	Thickness (μm)	Fiber Diameter (μm)	Air Permeability ($m^3/s/m^2$)	Shrinkage (%) MD	Shrinkage (%) CD	Filtration Efficiency (%)
1A	0.67	284.6	15.0	5.21	26.3	3.8	38.7
3A	0.67	269.4	7.9	2.24	11.8	3.3	48.1
3B	0.73	280.0	4.6	1.51	18.5	15.5	57.1
4A	0.74	228.2	7.5	1.77	38.8	13.8	67.3
4B	0.72	244.0	4.8	0.65	39.8	29.5	86.5

1A: 100% Dried Recycled PET Webs

3A: 80% Recycled PET/ 20% High I.V. PBT Webs

3B: 80% Recycled PET/ 20% Low I.V. PBT Webs

4A: 75% Recycled PET/ 25% Low I.V. PET Webs

4B: 50% Recycled PET/ 50% Low I.V. PET Webs

TABLE VIII

MECHANICAL PROPERTIES AND INTRINSIC VISCOSITY OF WEBS PRODUCED FROM BLENDS OF RECYCLED PET

Samples	Tenacity (mN/tex) MD	CD	Elongation (%) MD	CD	Bursting Strength (kPA)	Stiffness (mg.cm)	Intrinsic Viscosity (dl/g)
1A	6.12	3.40	44.0	96.0	21.1	83.5	0.60
3A	7.14	5.61	45.0	75.0	24.1	52.7	0.49
3B	8.53	4.81	27.7	41.5	31.4	39.3	0.48
4A	11.2	3.98	25.5	110.1	23.3	80.2	0.52
4B	10.8	4.08	16.5	62.0	34.4	65.8	0.51

1A: 100% Dried Recycled PET Webs

3A: 80% Recycled PET/ 20% High I.V. PBT Webs

3B: 80% Recycled PET/ 20% Low I.V. PBT Webs

4A: 75% Recycled PET/ 25% Low I.V. PET Webs

4B: 50% Recycled PET/ 50% Low I.V. PET Webs

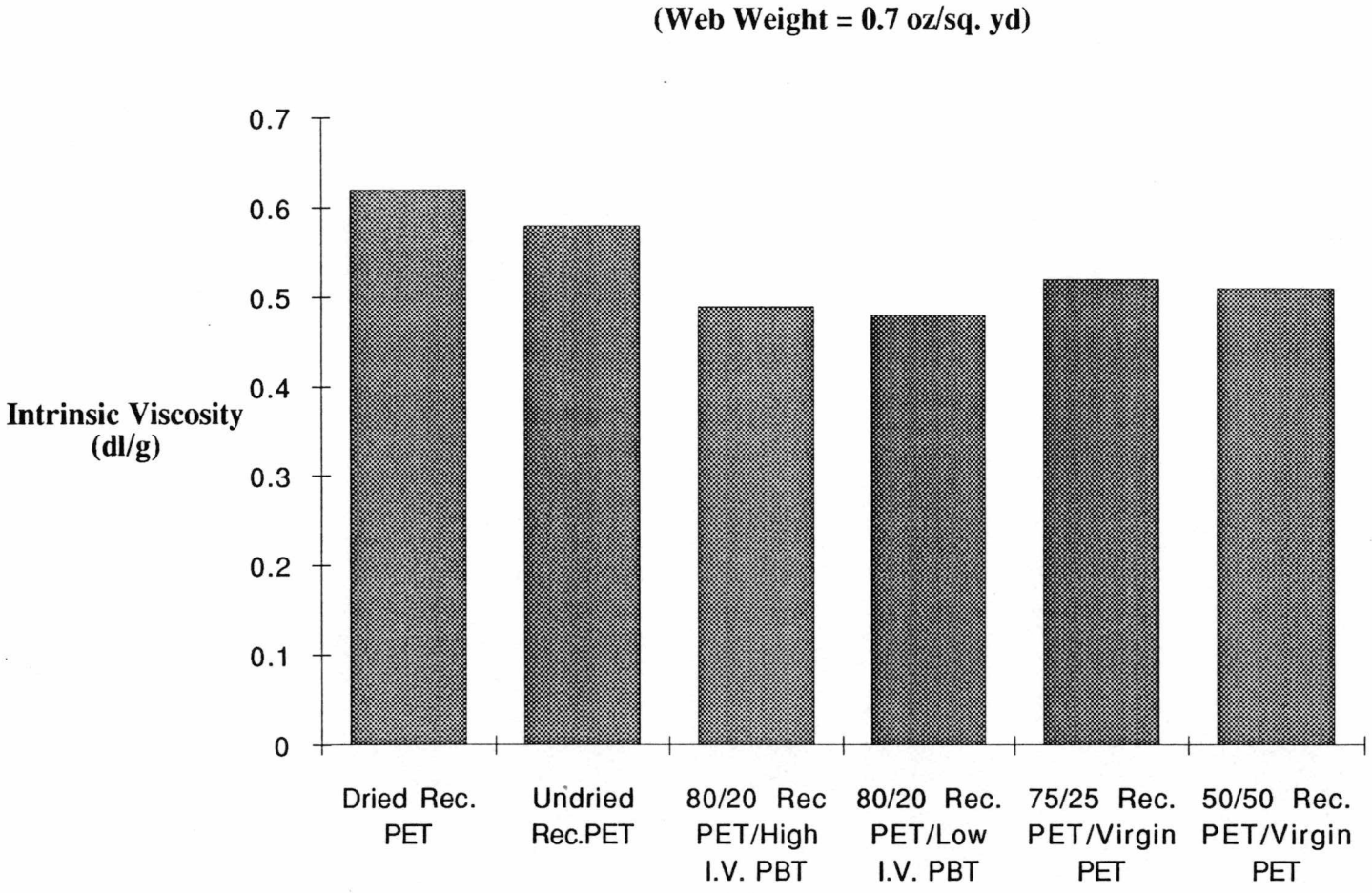


FIGURE IX. THE INTRINSIC VISCOSITY OF WEBS PRODUCED FROM RECYCLED PET AND ITS BLENDS

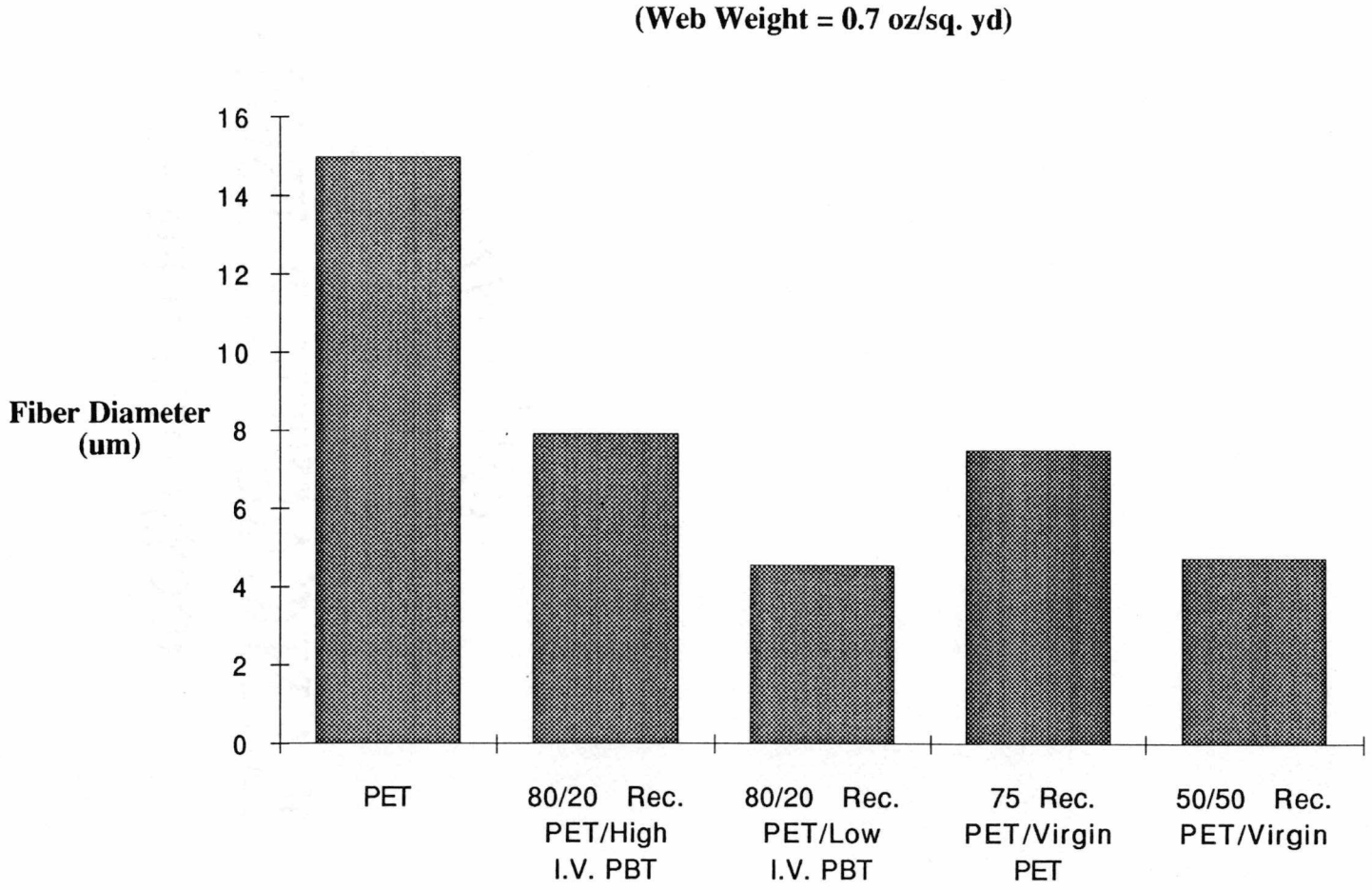


FIGURE X. THE FIBER DIAMETER OF WEBS PRODUCED FROM RECYCLED PET AND ITS BLENDS

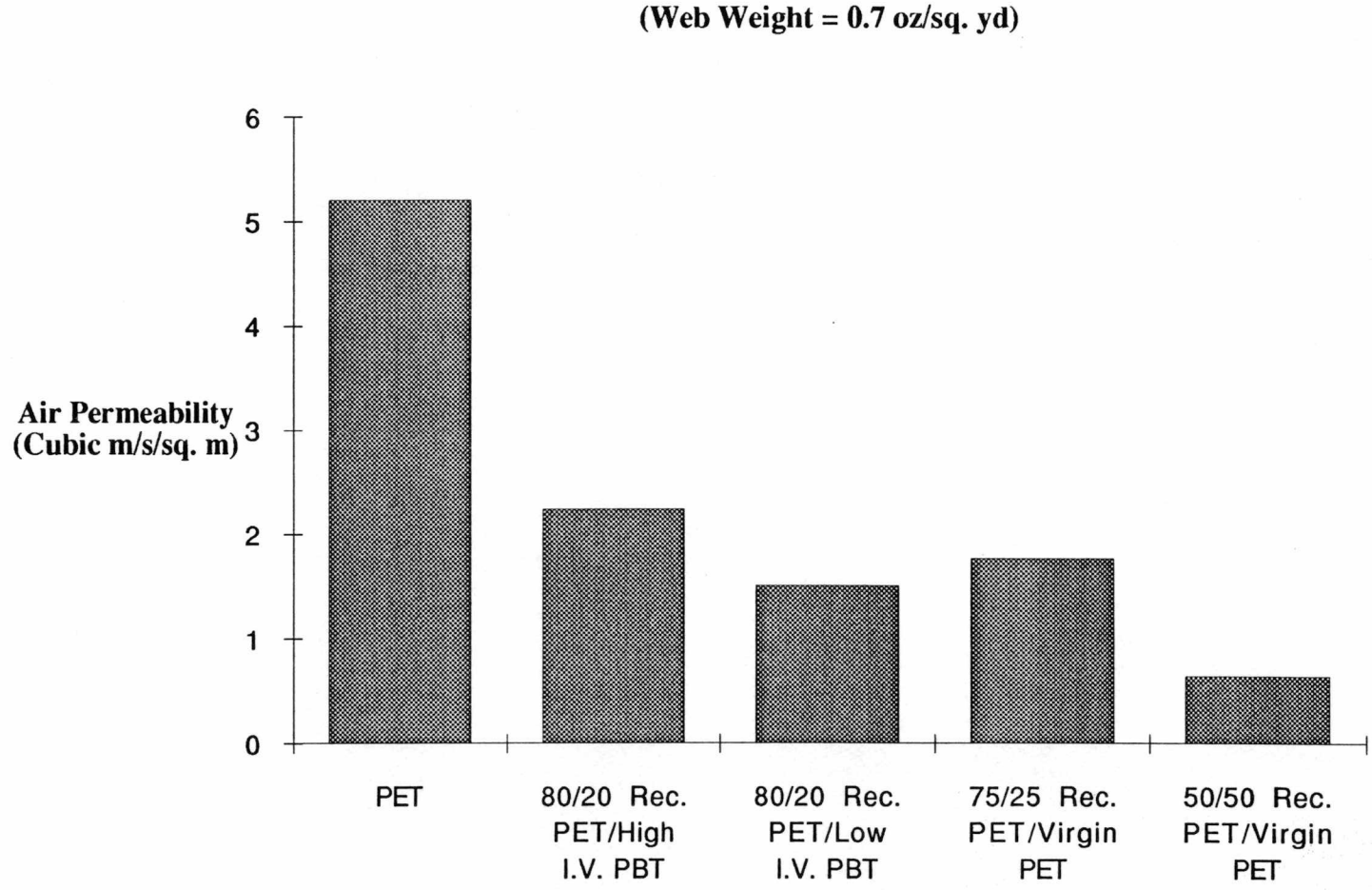


FIGURE XI. THE AIR PERMEABILITY OF WEBS PRODUCED FROM RECYCLED PET AND ITS BLENDS

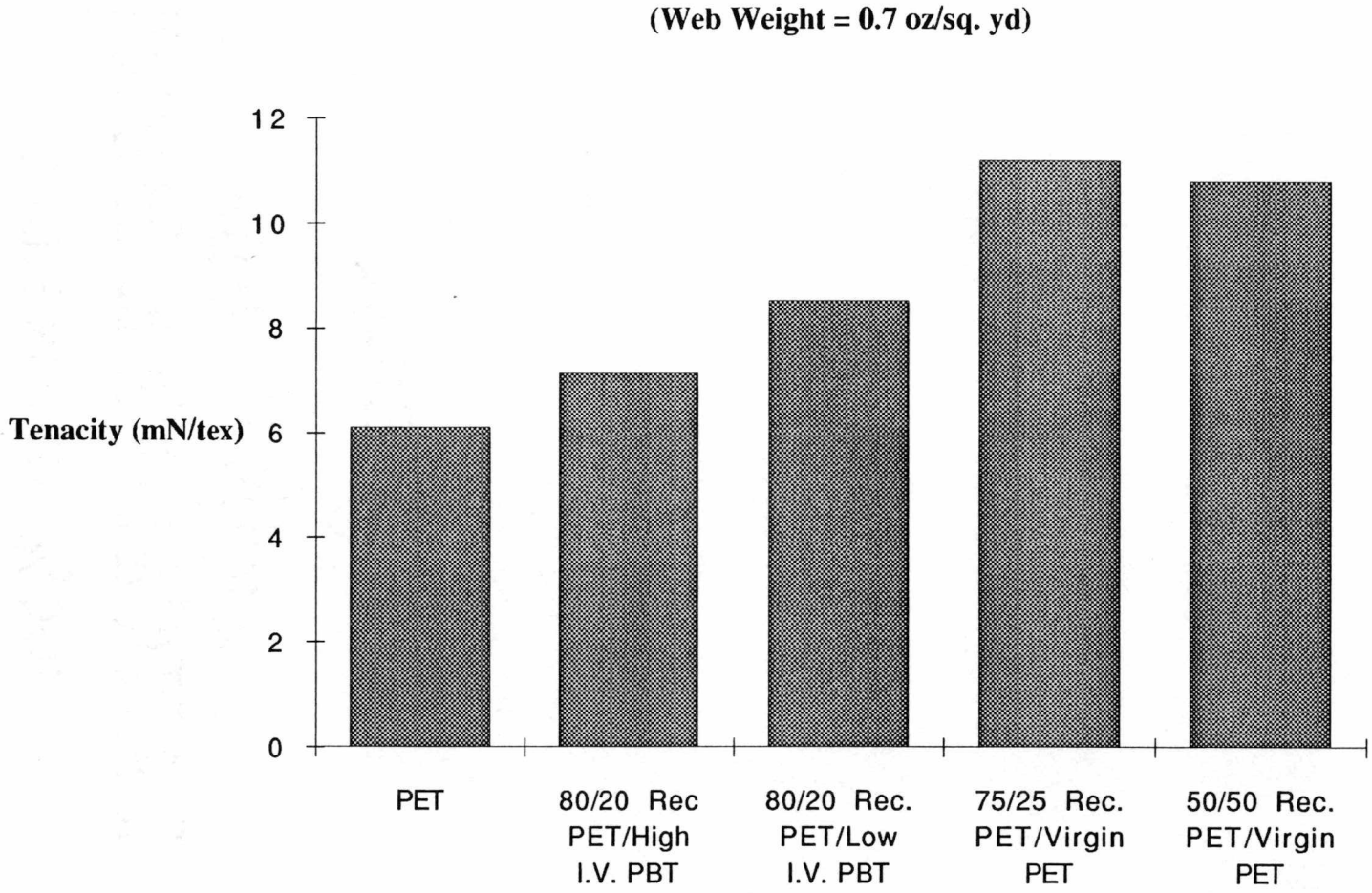


FIGURE XII. THE TENACITY IN MACHINE DIRECTION OF WEBS PRODUCED FROM RECYCLED PET AND ITS BLENDS

blending with more than 4% PBT could help in reducing the melt viscosity of PET. The result of the intrinsic viscosity was consistent with our expectation. The intrinsic viscosity of 100% recycled PET webs was 0.60 while the I.V.s of 80/20 recycled PET/high I.V. PBT webs and 80/20 recycled PET/low I.V. PBT webs were less than 0.5 (0.49 and 0.48 respectively). The lower intrinsic viscosity of PET/PBT blends contributed to lower fiber diameter, and consequently compact fibers in the web, which reduces the air permeability. Compact structure of fibers in the web also contributes to higher tenacity observed in the machine direction.

That the webs produced from recycled PET blended with low I.V. PET had lower intrinsic viscosity compared to that of 100% recycled PET (**Fig. IX**). The low I.V PET also aided in lowering the intrinsic viscosity of recycled PET. The intrinsic viscosity was lowered from 0.6 of 100% recycled PET webs to 0.52 of 75/25 recycled/virgin PET webs and 0.51 of 50/50 recycled/virgin PET webs. The webs produced from recycled PET/low I.V. PET blend also had lower fiber diameter (**Fig. X**), had less air permeability (**Fig. XI**), had higher tenacity in machine direction (**Fig. XII**), had higher filtration efficiency and higher shrinkage, and were thinner. It was also observed that the 50/50 recycled PET/virgin PET had more property changes than the 75/25 recycled PET/virgin PET.

The rheological properties of recycled PET and its blends were determined by using an Instron™ capillary rheometer. The results (**Fig. XIII**) showed that the virgin low molecular weight PET (Eastman Chemical Products Inc., Kingsport, TN) had the lowest melt viscosity and the blends of the recycled PET and the virgin PET had lower melt visco-

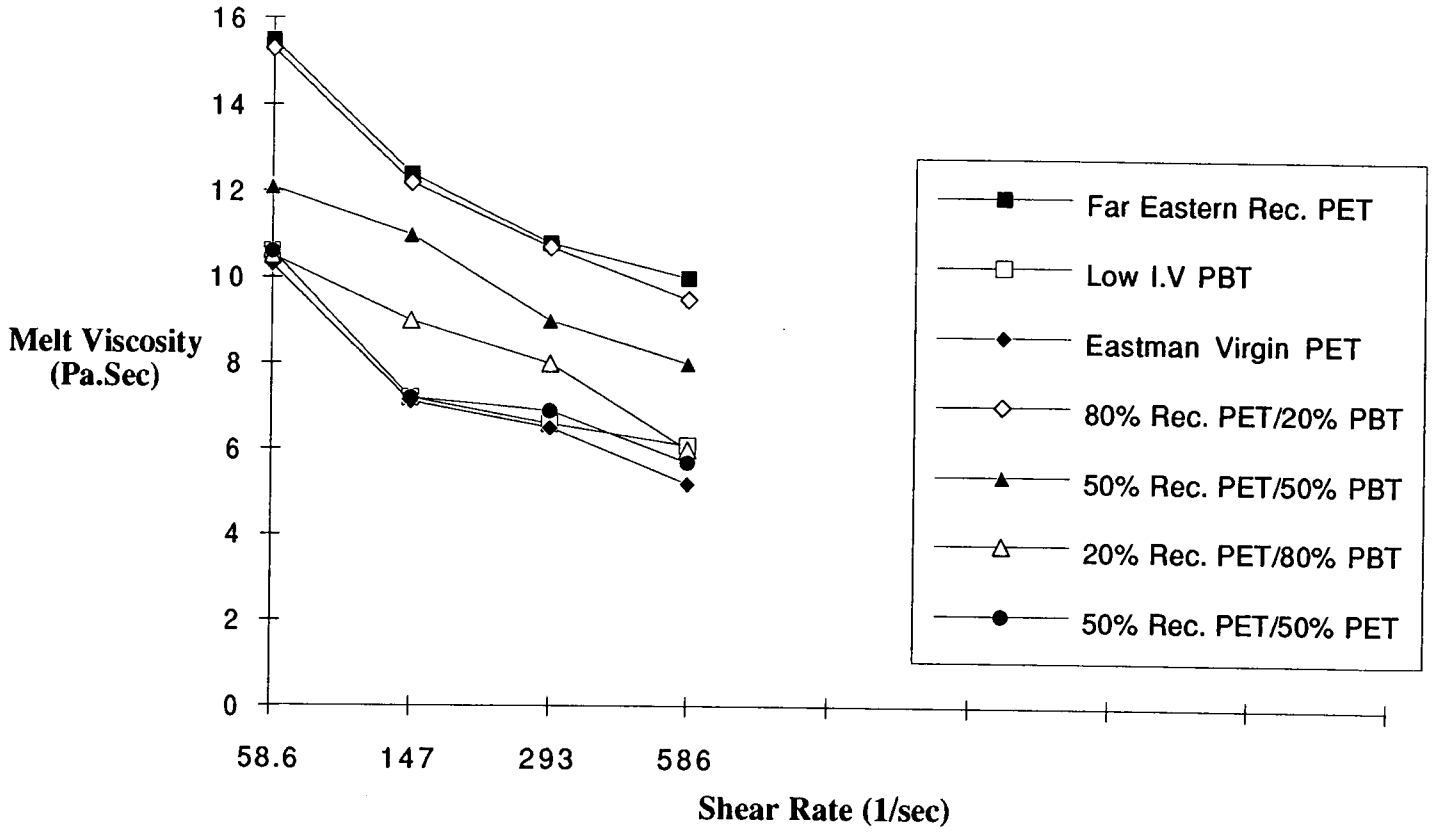


FIGURE XIII. THE MELT VISCOSITY OF RECYCLED PET AND ITS BLENDS (MEASURED AT 280 ^{O}C)

sity than 100% recycled PET polymer. Low I.V. PBT and the blends of recycled PET with low I.V. PBT also had lower melt viscosity than 100% recycled PET. It was also observed that among three PET/PBT blends, the 20/80 blends, which had more PBT, had lower melt viscosity than 50/50 and 80/20 PET/PBT blends.

Low I.V. PET used in this study was a virgin PET from Eastman Chemical Products Inc., which was tailored for the melt blown processing (I.V.= 0.62). Since the virgin PET and recycled PET do not have differences in chemical structure, it is possible to say that low I.V. recycled PET would have the same effect as the low I.V. virgin PET.

Using Higher Processing Temperature. The melt blown processing temperatures were increased in two ways: (1) increasing the die temperature and (2) increasing the heating zone temperatures gradually as well as, the die temperature. It was thought that the higher processing temperature would result in increased thermal degradation during the processing, which would lower the molecular weight of recycled PET. Recycled PET polymers from Far Eastern Textile Ltd. were processed under the processing conditions listed in **Table II.**

The properties of these two webs and the web produced at normal die and heating zone temperatures are listed in **Table IX** and **Table X.** There were no property improvements of the webs produced at the higher die temperature over the webs produced at normal temperature when only the die temperature was increased. The comparison pair (5A and 5B) with

TABLE IX

BASIS WEIGHT, THICKNESS, FIBER DIAMETER, AIR PERMEABILITY, SHRINKAGE AND FILTRATION EFFICIENCY OF WEBS PRODUCED AT HIGHER PROCESSING TEMPERATURE

Samples	Basis Weight ($oz/yard^2$)	Thickness (μm)	Fiber Diameter (μm)	Air Permeability ($m^3/s/m^2$)	Shrinkage (%) MD	CD	Filtration Efficiency (%)
5A (1B)	1.15	312.6	13.9	1.38	35.3	11.3	50.5
5B	1.15	431.6	14.2	2.03	16.3	10.3	49.3
5C	1.16	296.0	8.5	1.02	16.0	10.3	57.1

5A: Dried Recycled PET Webs Produced at Normal Processing Temperature

5B: Dried Recycled PET Webs Produced at Increased Die Temperature

5C: Dried Recycled PET Webs Produced at Increased Heating Zone and Die Temperature

TABLE X

MECHANICAL PROPERTIES AND INTRINSIC VISCOSITY OF WEBS PRODUCED AT HIGHER PROCESSING TEMPERATURE

Samples	Tenacity (mN/tex)		Elongation (%)		Bursting	Intrinsic
	MD	CD	MD	CD	Strength (kPA)	Viscosity (dl/g)
5A (1B)	9.83	6.91	50.0	95.0	34.5	0.60
5B	9.22	5.67	35.0	60.0	35.0	0.60
5C	12.6	6.68	54.5	135.0	37.5	0.58

5A: Dried Recycled PET Webs Produced at Normal Processing Temperature

5B: Dried Recycled PET Webs Produced at Increased Die Temperature

5C: Dried Recycled Webs Produced at Increased Heating Zone and Die temperature

similar basis weight had similar fiber diameter, air permeability and bursting strength. The web produced using higher die temperature had lower tenacity in both machine and cross directions.

During the melt blown processing, the polymer was heated and melted when it went through the heating zones of the extruder, in which every heating zone was set to a higher temperature than the previous zone, and finally blown by hot high-velocity air to the collector screen to form a web. The intrinsic viscosity did not decrease more than in the case of regular die temperature when only the die temperature was increased. The reason could be that the time that the polymer stayed in the die was very short, and the polymer did not have enough time to reach the increased die temperature.

The web produced at higher heating zone temperatures as well as, higher die temperature (5C) had a slightly lower intrinsic viscosity (0.58) than the web (5A) produced at normal processing temperature (0.60). The fiber diameters and air permeability of 5C (8.5 and 1.02 $m^3/s/m^2$) were also notably lower than those of 5A (13.9 and 2.10 $m^3/s/m^2$), although they had similar basis weight. The tenacity in machine direction of 5C was increased to 12.6 mN/tex from 9.83 mN/tex of 5A (**Table X**). The tenacity in cross direction, elongation and bursting strength of these two webs had no obvious differences.

During the processing using increased heating zone temperatures and die temperature, the polymer was hotter and had a lower viscosity at the die. The temperature difference between the last heating zone and the die

was not as great as in the previous method, which made it possible for polymer to reach the die temperature before it left the die. The only difference between the two processing runs was the processing temperatures, indicating that the higher temperature was responsible for the web property changes. The drop in the intrinsic viscosity confirmed the prediction, i.e., more thermal degradation occurred during processing. The thermal degradation contributed to the finer fibers, lower air permeability and high tenacity in machine direction of the webs produced using higher processing temperature.

Heat Setting. The melt blown webs had shrinkage values as high as 40% (50/50 recycled/virgin PET). Higher shrinkage limits their usage to low temperature conditions. In an attempt to reduce the thermal shrinkage, three heat setting conditions (125 °C, 3 minutes; 150 °C, 3 minutes; 150 °C, 5 minutes) were tried and the resultant webs were evaluated.

The properties of the webs before and after heat setting are listed in **Table XI** and **Table XII**. On heat setting, the thermal shrinkage in both machine and cross direction of these three webs was considerably reduced. After heat setting at 125 °C for 3 minutes, shrinkage was less than 2.5%; and after heat setting at 150 °C for 3 minutes, shrinkage was less than 1% (**Fig. XIV**). The thickness of these webs also decreased (**Fig. XV**) and the tenacity in the machine direction increased (**Fig. XVI**).

TABLE XI.

SHRINKAGE, THCIKNESS AND STIFFNESS OF WEBS BEFORE AND AFTER HEAT SETTING

Samples	Conditions	Shrinkage (%) MD	Shrinkage (%) CD	Thickness (um)	Stiffness(mg.cm) MD	Stiffness(mg.cm) CD
6A	Before H.S	38.8	13.8	228.2	12.8	58.5
	(125 °C, 3 Min)	1.5	2.3	175.0	28.7	64.7
	(150 °C, 3 Min)	<0.1	<0.1	159.8	28.7	86.5
	(150 °C, 5 Min)	<0.1	<0.1	160.3	34.8	94.7
6B	Before H.S.	8.8	8.9	520.3	83.5	240.9
	(125 °C, 3 Min)	0.6	1.3	441.0	121.5	278.8
	(150 °C, 3 Min)	<0.1	<0.1	420.4	189.4	348.2
	(150 °C, 5 Min)	<0.1	<0.1	418.9	243.6	404.3
6C	Before H.S.	36.3	19.4	301.2	49.3	264.4
	(125 °C, 3 Min)	1.2	1.4	259.3	61.6	281.8
	(150 °C, 3 Min)	<0.1	<0.1	221.0	96.0	352.9
	(150 °C, 5 Min)	<0.1	<0.1	219.5	93.7	402.4

6A: 75% Recycled PET/ 25% Low I.V. PET Webs

6B: 75% Recycled PET/ 25% Low I.V. PET Webs

6C: 100% Recycled PET

TABLE XII.

TENACITY, ELONGATION AND BURSTING STRENGTH OF WEBS BEFORE AND AFTER HEAT SETTING

Samples	Conditions	Tenacity (mN/tex) MD	Tenacity (mN/tex) CD	Elongation (%) MD	Elongation (%) CD	Bursting Strength(kPA)
6A	Before H.S	11.2	4.0	25.5	110.0	23.3
	(125 °C, 3 Min)	11.9	6.9	9.1	24.1	19.3
	(150 °C, 3 Min)	9.9	4.1	3.0	3.0	7.8
	(150 °C, 5 Min)	8.4	4.1	3.0	3.0	3.4
6B	Before H.S.	10.6	4.6	19.5	109.5	24.1
	(125 °C, 3 Min)	15.6	9.0	29.0	35.5	21.4
	(150 °C, 3 Min)	9.8	5.4	3.0	2.5	3.4
	(150 °C, 5 Min)	8.5	6.4	3.0	3.0	1.7
6C	Before H.S.	6.1	3.5	15.1	82.5	15.5
	(125 °C, 3 Min)	8.8	5.4	11.0	17.0	13.3
	(150 °C, 3 Min)	7.2	4.2	1.5	1.0	3.4
	(150 °C, 5 Min)	6.4	4.0	1.8	1.0	3.4

6A: 75% Recycled PET/ 25% Low I.V. PET Webs

6B: 75% Recycled PET/ 25% Low I.V. PET Webs

6C: 100% Recycled PET

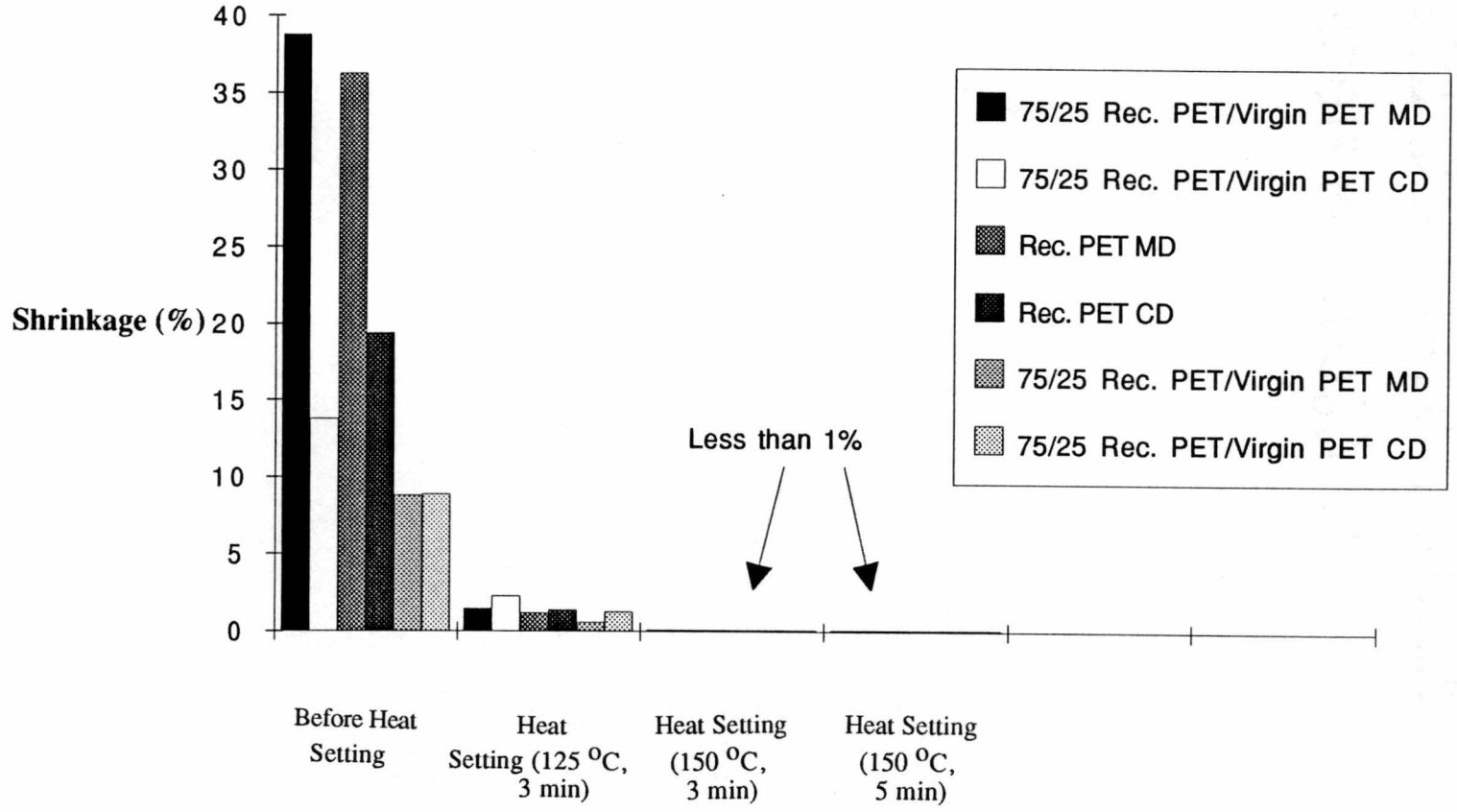


FIGURE XIV. THE SHRINKAGE OF WEBS BEFORE AND AFTER HEAT SETTING

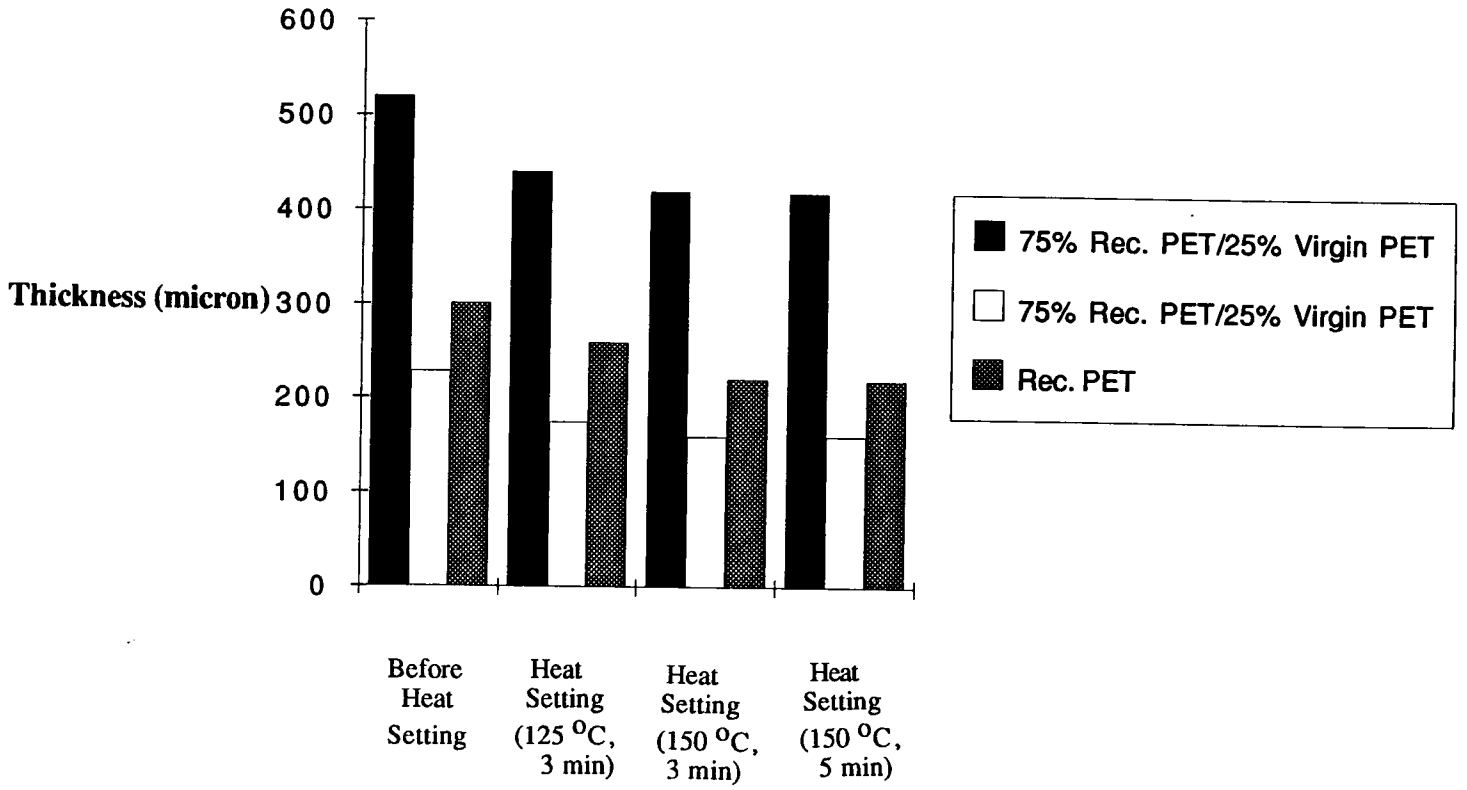


FIGURE XV. THE THICKNESS OF WEBS BEFORE AND AFTER HEAT SETTING

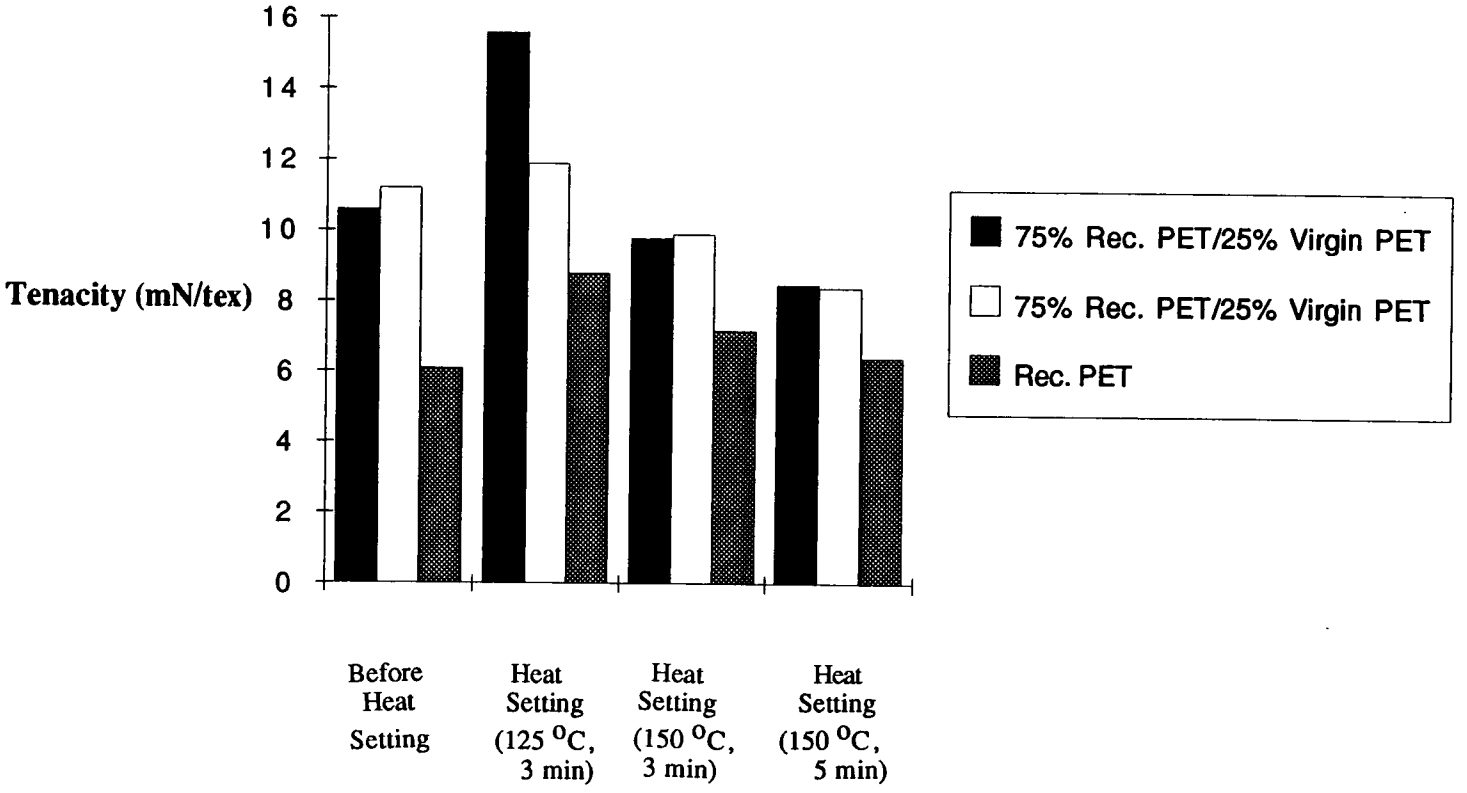


FIGURE XVI. THE MD TENACITY OF WEBS BEFORE AND AFTER HEAT SETTING

DSC scans of webs before and after heat setting (**Fig. XVII**) indicated the crystallization occurred in the amorphous regions of the fibers during heat setting. The area under the crystallization peak (around 115 ^{o}C), which reflects the potential crystallizing capacity of the fiber, was minimized and finally eliminated after heat setting at 150 ^{o}C for 5 minutes. The DSC results indicated that the oriented, non-crystalized regions in the fibers, which contributes to thermal shrinkage, crystallized during the heat setting.

The web dimensions were held constant during heat setting. The initial increase in the tenacity in machine direction was probably due to the more compact web and resistance of the fibers to move. The drop of the tenacity in the heat setting may be due to that the webs become stiffer and more brittle after being exposed to heat setting temperatures. The results indicate that, of the three heat setting conditions studied, 125 ^{o}C and 3 minutes may be sufficient if a small shrinkage (up to 3.0%) is tolerable. It is possible to achieve the same results using less time and higher temperature. Nevertheless, the results showed that heat setting can be used to decrease the shrinkage of melt blown PET webs.

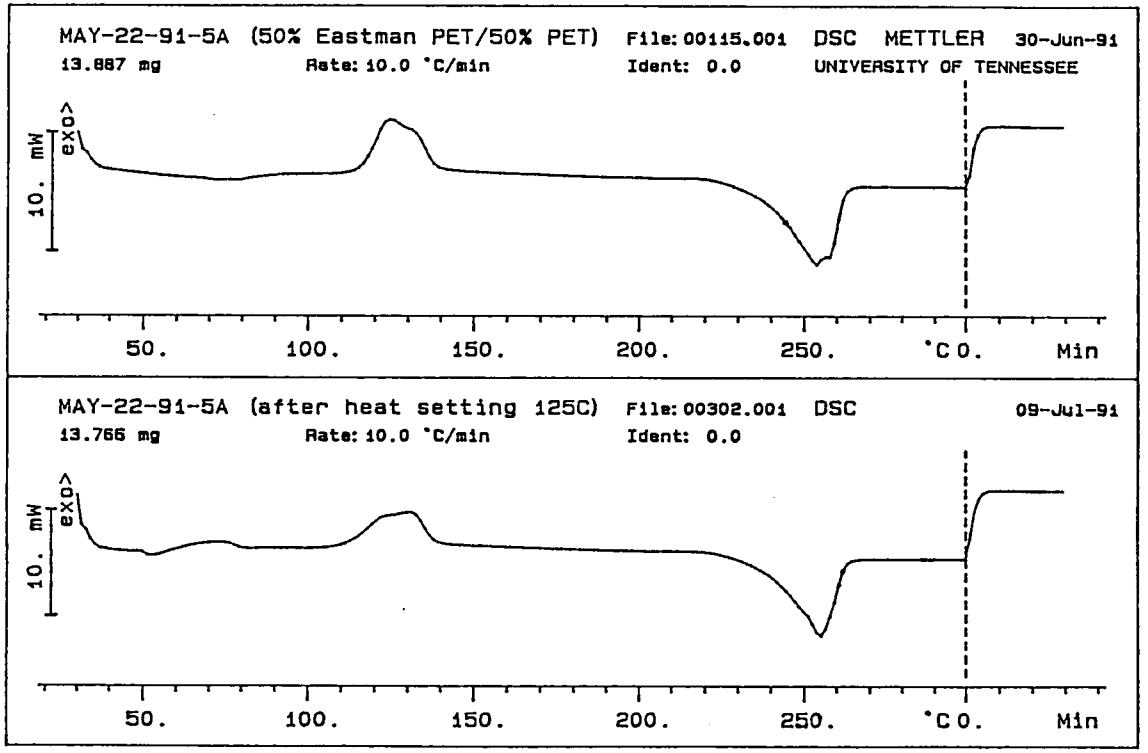


FIGURE XVII. THE DSC RESULTS OF THE MELT BLOWN WEBS BEFORE AND AFTER HEAT SETTING

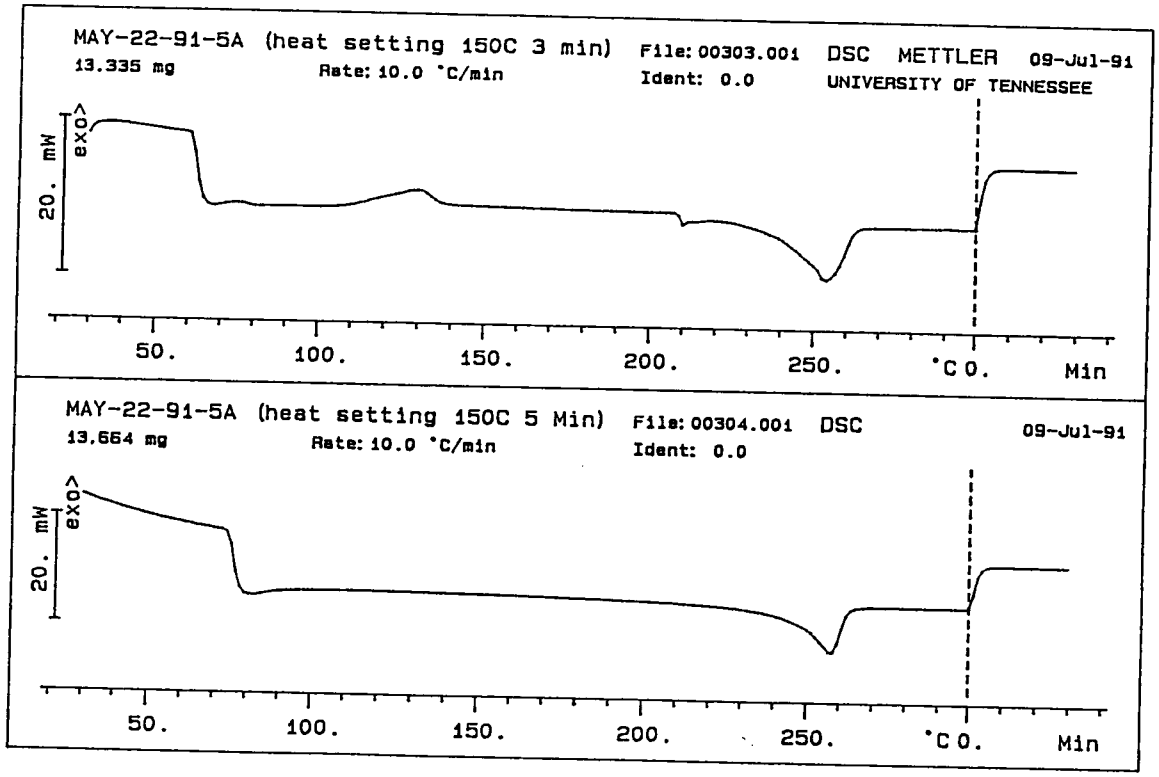


FIGURE XVII. (CONTINUED)

CHAPTER V

CONCLUSIONS

The objectives of this research were to evaluate three methods of improving the melt blown processing of recycled PET and to study the effects of heat setting on the properties of melt blown webs. The three methods that were studied in this research were: (1) using undried recycled PET polymer instead of the dried polymer; (2) blending the recycled PET with other polymers (PBT and low I.V. PET); and (3) processing the recycled PET at higher temperatures. Some of the webs that showed very high thermal shrinkage were heat set under three different conditions (125 ^{o}C, 3 minutes; 150 ^{o}C, 3 minutes; 150 ^{o}C, 5 minutes). The properties of the webs before and after heat setting were evaluated.

The difference between dried and undried PET was the moisture content. The webs produced with undried PET, which had more moisture (0.263% than dried PET (0.00713%), had lower intrinsic viscosity, smaller fiber diameters and a more compact web structure, higher tenacity in the machine direction and lower air permeability. The greater drop in intrinsic viscosity indicated that more hydrolytic degradation occurred during processing for undried PET. The lowered intrinsic viscosity resulted in lower fiber diameter and compact web structure, which contributed to lower air permeability and higher tenacity in the machine direction. The dried and undried PET webs had different load-elongation curves, which showed that the undried PET webs had higher initial modulus.

The recycled PET (I.V. = 0.82) was blended with two grades of virgin PBT (I.V. = 0.88 and I.V. = 0.77) and a low I.V. virgin PET (I.V. = 0.62). The webs produced from blends of PET and PBT had lower intrinsic viscosity, smaller fiber diameters, lower air permeability and higher tenacity in machine direction than those of 100% recycled PET webs. The drop in the intrinsic viscosity caused by blending PBT with PET was consistent with the previous studies [6-9].

The webs produced from the recycled PET and low I.V. virgin PET blend had lower intrinsic viscosity, smaller fiber diameters, lower air permeability, higher tenacity in machine direction and higher filtration efficiency. The webs were thinner. It was also observed that the greater the amount of the low I.V. PET in the blend, the greater the property changes in the webs. The lower molecular weight of low I.V. PET decreased the molecular weight of the recycled PET and low I.V. virgin PET blends, which led to a decrease in apparent viscosity.

Two different methods of increasing the processing temperature were explored: (1) increasing only the die temperature; (2) increasing the heating zone temperatures gradually as well as increasing the die temperature. There were no notable property changes caused by the former method. The webs produced by the later method however, had lower intrinsic viscosity, smaller fiber diameters, lower air permeability and higher tenacity in machine direction, and the webs were thinner.

The effect of heat setting on the properties of melt blown webs was studied by heat setting three melt blown webs under three different condi-

tions. Through heat setting, the shrinkages of webs were considerably reduced (within 1%, after heat setting at 150 ^{o}C for 3 minutes, compared to 40% without heat setting). Because webs were heat set under a dimensional constraint, there were no length and width changes. The thickness of the webs was reduced, resulting in more compact web structure. The tenacity in the machine direction increased when the webs were heat set at low temperatures for a short time, and when the heat setting temperature and time further increased, the tenacity in the machine direction decreased. The DSC results of the webs before and after heat setting showed a reduction of the totally uncrystallized region in the fibers after heat setting. Crystallization of these regions resulted in elimination of thermal shrinkage on heat setting.

It was observed that all these three approaches ((1) using undried recycled PET instead of dried one; (2) blending recycled PET with other polymers; and (3) increasing processing temperatures) helped in decreasing the melt viscosity of the recycled PET during the melt blown process, which lead to an improvement on the performance of the webs produced. All three approaches have their advantages and drawbacks. Using undried recycled PET is simple and inexpensive, and the improvement of the web performances is obvious. Its drawback however, is the difficulty of controlling the moisture content in the polymer. The amount of moisture determines the extent of hydrolytic degradation and property changes. Thus it will result in the difficulty of predicting the performance of the final webs. Blending is a straightforward and inexpensive way to improve

the properties of the polymers. Because the performance of the final webs is determined by the blend ratios and the properties of the polymers and processing conditions, it is predictable and easier to control. Increasing the processing temperatures can cause more thermal degradation, resulting in lower melt viscosity. The limitation of this approach is the capability of the equipment. The high extent of thermal degradation may also cause changes in appearance (discoloration) of the melt blown webs. The cost of processing will also increase when the polymer has to be processed at higher temperatures.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE WORK

In this study, the effect of moisture in PET during melt blown processing was studied. It was observed that the higher moisture content in the undried recycled PET could help in decreasing the apparent viscosity of recycled PET, and the fiber diameters could be lowered from 15 μm to about 9 μm. Further study on the effects of higher moisture contents to decrease the molecular weight of recycled PET is recommended. Through optimization of the processing conditions and increased moisture content of recycled PET, the fiber diameter of recycled PET webs can be decreased.

It was observed in this study that PBT aided in decreasing the apparent viscosity of PET/PBT blends. It is recommended that different ratios of PET/PBT blends be tried, so that an optimal blending ratio of recycled PET and PBT can be determined. Also using PBT with an I.V. less than 0.7, if available, is recommended. With lower I.V. PBT, sufficient reduction in melt viscosity can be achieved with smaller loadings.

The PBT and low I.V. PET used in this study were virgin polymers. It is predicted that the recycled PBT and recycled low I.V. PET of similar intrinsic viscosities would have the same effect. Further studies using recycled PBT and recycled low I.V. PET are recommended.

More thermal degradation was observed in melt blown processing using higher heating zone and die temperatures. No obvious color change

because of degradation was observed in the webs, which suggested that further increase in the processing temperature is possible. It should be possible to increase the temperatures in the last heating zone of the extruder and at the die and achieve further reduction in melt viscosity. It is also recommended that processing aids such as plasticizers, which may be able to lower the apparent viscosity of the recycled PET during melt blown processing, be used in future studies.

Heat setting of melt blown webs served to decrease the thermal shrinkage. It was observed that the properties of the heat set webs depended on the heat setting temperature and time. It is recommended that these two heat setting parameters be optimized.

Because there was no force feeding system on the melt blown processing line at UTK, feeding problems occurred when polymer flakes were processed. It is suggested that these experiments in this study be repeated on the melt blown processing line with forced feeding system for the polyester flakes.

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VITA

Yi-xiang Zhang was born in Shanghai, China, on February 20, 1966, to Mr. and Mrs. Yuqi Zhang as their second son. He graduated from The Affiliated High School of Shanghai Normal University, Shanghai, in 1984. He attended China Textile University, Shanghai, China from 1984 to 1988. In July, 1988 he received a Bachelor of Science degree in Textile Material Science from the China Textile University as an honor graduate. He worked in Shengzhen, GuangDong, China from 1988 to 1989. In January, 1990 he entered the Graduate School at The University of Tennessee, and was awarded a Graduate Teaching Assistantship. In October, 1990 he was awarded a Graduate Research Assistantship from the Consortium Project of Melt Blown and Spunbond Nonwovens from Recycled Polymers, which was sponsored by five domestic and international companies including Exxon Chemicals Company. In December 1991, he received a Master's degree in Textile Science.