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THE EFFECT OF RECYCLED LOW DENSITY POLYETHYLENE SUBSTITUTED IN VIRGIN LINEAR LOW DENSITY POLYETHYLENE AS POLYMER BLENDS ON MECHANICAL PROPERTIES

By

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ABSTRACT

THE EFFECT OF RECYCLED LOW DENSITY POLYETHYLENE SUBSTITUTED IN VIRGIN LINEAR LOW DENSITY POLYETHYLENE AS POLYMER BLENDS ON MECHANICAL PROPERTIES

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Binary blends were prepared from recycled low-density, and virgin linear low-density polyethylene. The blends have been evaluated in terms of seal strength, tensile stress-strain behavior, impact resistance, tear resistance, and crystalline melt temperature. Mechanical and thermal data were collected in order to evaluate the influence of recycled LDPE content in the blends on these properties. The phase behavior of the blend cannot be predicted from this investigation. The tensile properties, tear resistance, and impact resistance show variations with composition and are intermediate between those of the parent polymers. The addition of recycled LDPE decreases some mechanical properties, however it can be added at a certain concentration without significantly reducing such mechanical properties of virgin LLDPE. Such blends may have practical utility by yielding materials having a combination of strength, stiffness, and toughness.

To my mother, Sirirat Nilagupta and my father, Pramuan Nilagupta

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CHAPTER I

INTRODUCTION

Polyethylene is a thermoplastic and is the leader in total resin sales. Polyethylene film is the lowest cost and most common plastic packaging material. In 1984, 5.4 billion lbs. [16] of low-density polyethylene (LDPE) went into readily disposable consumer packaging, such as trash bags, grocery sacks, shrink and stretch film. These products finally ended up in the waste stream. Linear low-density polyethylene (LLDPE) acquired commercial importance because of its superior mechanical behavior compared to LDPE. Blends of LDPE and LLDPE are now regarded as excellent materials for film manufacture because they combine the processability of LDPE and good mechanical properties of LLDPE [1]. As the LDPE recycling rate begins to grow, this research investigates regarding the resulting mechanical properties when recycled LDPE is blended with virgin LLDPE at different concentration levels.

1.1 Industrial Plastic Scrap and Recycling

Recycling has become a very critical issue to everybody. The volume of solid waste has been increasing continuously for several decades. Landfill is no longer the most efficient way to dispose of solid waste because there are fewer sites and higher costs. Incineration, another method of waste disposal, is also costly and pollutes the environment. Recycling seems to be an appropriate solution to reducing the volume of solid waste to be landfilled and incinerated.

Among the materials in the waste stream, plastics are a very visible proportion and are perceived by the public as an environmental problem. It is expected that plastics will represent 19.9% of landfill volume by the year 2000 [7].

No certain figure of the industrial plastic produced or discarded each year has been reported. In the plastics industry, material cost is a major factor of the cost of final products. Reuse of any recoverable materials such as reject products, offcuts, sprues, runners, flash and tops, tails of bottles, and trimming is an economic necessity. The higher cost of petroleum feedstock has increased the value of plastics to where its reincorporation into plastic has become more attractive.

Recycling of homogeneous scrap is relatively easy in the early stages of plastic production and converting, where it can occur internally within one manufacturing organization. Recycling is very much more difficult in the final stage, mixed with heterogeneous consumer waste. Markets for industrially generated plastic scrap are more established than for post-consumer.

The in-plant scrap is that generated in manufacturing processes, production, fabrication, and converting, usually is free of contaminants. The scrap can be reprocessed by the manufacturer or by an independent firm. It can either be sold back to the generating industry or to another industry as a replacement for virgin material, or it can be sold as a lower grade material. Provided price and technical requirements can be met, there are many end market uses that can be satisfied with recycled material, for instance, recycling LDPE film into plastic garbage bags, or recycling PVC (polyvinylchloride) auto trim scrap into trunk mats for use in the auto industry [16]. Recycled plastics must be cheaper than virgin plastics to be considered as a potential source of supply for any manufacturer. At a minimum, for recycled material to gain acceptance its price must be 25% less than prime grade virgin material [16]. The assurance of clean uncontaminated quality recycled material is as important to users as is price. Plastic processors generally cannot tolerate more than 1 to 5% contamination levels acceptance [16]. The quality must be consistent and the material guaranteed homogeneous. It is for these reasons that industrial sources of waste plastic supply are the preferred source for most reprocessors. In terms of plastic recycling, reprocessing of uncontaminated plastic with virgin material, back into the same forming process or plastic product from which it came, is considered primary recycling.

1.2 Why Polymer Blends

Mixing polymers to achieve an economic or property advantage is not a new idea. The scientific and commercial progress in the area of polymer blends during the past two decades has been tremendous.

Several driving forces have spurred the intense interest of polymer suppliers in developing polymer blends. Polymer blends provide materials that are tailored to specific application requirements, with performance that could not be duplicated by an existing single polymer. Blending can improve physical, mechanical, and permeability properties, chemical resistance, thermal-performance, and processability of polymers. It is more convenient, less expensive, and less time consuming for the plastics producers and compounders to develop new blended products than to develop totally new polymers. Raw materials and manufacturing equipment for blends are generally available to suppliers from their other product lines (for example, an extruder is often used as the reactor), thereby reducing development risks.

Recycling is another important reason to blend plastics. Adding the plastic scrap, in pellet form, to the virgin resin can reduce raw material cost.

The forces driving the development of polymer blends are not only from the suppliers; the growing demand for polymer-polymer mixtures is also a driving force. The engineering polymer alloys and blends represent one of the fastest growing polymer classes, with annual growth expected to average 9% annually [10]. It is expected that by the year 1995, engineering polymer alloys and blends will represent approximately 25% of the 1.1 billion kg. (2.5 billion lbs.) projected U.S. demand [10].

The plastics industry is committed to recycling. Various plastic products will be legislated out of the market unless they are being recycled, or have recycled content. Since polyolefins are the most commonly used plastics, they predominate in plastics waste. Because of the similarity in the chemical structures of LDPE and LLDPE, their recycling leads to mixtures without separation. Therefore, it is interesting to study the use of scrap LDPE as a substitute for virgin LLDPE in a polymer blend.

The objectives of this study are:

1. To study the effect on mechanical properties of % Recycled LDPE substitution for LLDPE in a polymer blend.

2. To predict the phase behavior of LDPE/LLDPE blends.

3. To determine the % recycled LDPE that can be added to the blend without significantly reducing the LLDPE properties.

CHAPTER II

REVIEW OF THE LITERATURE

In the initial stage in development of polymer blends, studies in polymer physics were involved with the understanding of the basic properties of homopolymers. Morphology and properties of low density and linear low density polyethylene (LDPE and LLDPE) are reviewed at the beginning of this chapter. The following reviews cover the basic aspects of polymer blends, for instance, miscibility, thermodynamics, mechanical properties, and compatabilizing agents. The previous studies about the blends of LDPE/LLDPE are reviewed at the end of this chapter.

2.1 Polyethylene

The various types of polyethylene are distinguished in terms of their density and structure as low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high density polyethylene (HDPE). The different densities result from a variation in the crystalline packing ability of polyethylenes due to a difference in their level of branching. The properties and morphology of only low and linear low-density polyethylene will be reviewed in this chapter.

Low-Density Polyethylene (LDPE)

Low-density polyethylene is a thermoplastic obtained through the high temperature (100 to 250 degree celsius) and high pressure (100 to 300 Mpa) free radical polymerization of ethylene [4]. This process produces rather frequent long-chain branching, about 15 to 20 ethyl (and a few butyl) side-chains per 100 carbon atoms in the main-chain [6]. The chemical structure of LDPE is irregular due to the long-chain branching. The spherulites in LDPE are markedly smaller than those in LLDPE of similar density and melt flow index [18]. The percent crystallinity is a function of the amount of short-chain branching and normally falls around 30 to 40% [10]. The density of LDPE falls between 0.918 to 0.932 gm/cc [11].

LDPE is a low cost material. It is used as a film as a major application. It exhibits good clarity, strength, flexibility, sealability, processability, ease of extrusion, low taste and odor transfer properties, and chemical inertness. It has moderate oil and grease resistance, but has good moisture barrier properties.

Linear Low-Density Polyethylene (LLDPE)

Linear low-density polyethylene is produced at much lower temperatures and pressures than low-density polyethylene. It is a copolymer of ethylene with large amounts (8 to 16%) of such higher alpha olefins as 1-butene, 1-hexene or 1-octene. These copolymers have short-chain branching characteristic of high-pressure polyethylene but have no long-chain branching [11]. Because of its linear structure and the absence of long-chain branching, LLDPE forms a more highly crystalline structure than LDPE. The spherulitic structure of LLDPE is more regular and consists of larger units relative to that of LDPE. The density of linear low-density polyethylene is between 0.910 to 0.925 gm/cc [11].

LLDPE has acquired great commercial importance because of its superior mechanical behavior (such as tensile strength, stiffness, toughness, impact properties, and tear properties) compared to LDPE. It is also a low cost material. It is a better moisture barrier than LDPE. One property where LLDPE suffers relative to LDPE is clarity. The haze and gloss of LLDPE film is poor [11].

Table 1: Processing and Mechanical Properties of Low Density Polyethylene and Linear Low Density Polyethylene [11]

Properties	Low density polyethylene	Linear low density polyethylene
1. Crystalline melt temp. (^{o}c)	98 - 115	122 - 124
2. Tensile yield strength (psi)	1300 - 2100	1400 - 2800
3. Tensile strength at break (psi)	1200 - 4500	1900 - 4000
4. Tensile modulus (X 1000 psi)	25 - 41	38 - 75
5. Percent elongation at break (%)	100 - 650	100 - 965
6. Dart drop (N/mm)	29 - 76	39 - 97

2.2 Polymer Blends

Polymer blends refer to intimate mixture of two or more polymers. They are physical mixtures of chemically distinct polymers that could exhibit homogeneous or heterogenous characteristics on a microscopic scale, but should not exhibit any obvious inhomogeneity on a macroscopic scale.

2.3 Polymer Miscibility

Polymer blends can be characterized by their phase behavior as being miscible, partially miscible, and immiscible.

1. Miscible polymer blend: appears homogeneous on a macroscopic level and is potentially useful for industrial application. It consists of one amorphous phase, as shown in Figure 1a. It is

much like a random copolymer in properties and processing. Among high-molecular weight polymers, on the other hand, the requirements of similarity in structure and/or polarity are so stringent that very few combinations of polymers have any appreciable miscibility, and miscible blends of two polymers are quite rare. Besides, some attraction between two polymers must be present to partially overcome the intramolecular cohesive forces of the individual polymers. Interpolymer attractions result from specific interactions between functional groups on polymer A with different functional groups on polymer B. Miscible blends will have a single, composition dependent, glass transition temperature (T_g). T_g can be calculated with the Gordon-Taylor expression [9]:

$$T_g = W_a T_{ga} + W_b T_{gb}$$

T_g is the glass transition temperature of the blend

T_{ga} and T_{gb} are the glass transition temperature of polymers A and B respectively

W_a and W_b are respective weight fractions of polymers A and B in the blend

The glass transition temperature can also be predicted based on the Fox equation [9]:

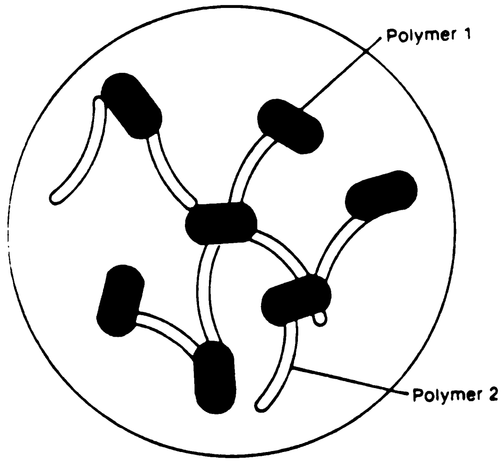
$$\frac{1}{T_g} = \frac{W_a}{T_{ga}} + \frac{W_b}{T_{gb}}$$

The Fox equation predicts that the T_g of the blend is somewhat lower than does the Gordon-Taylor equation.

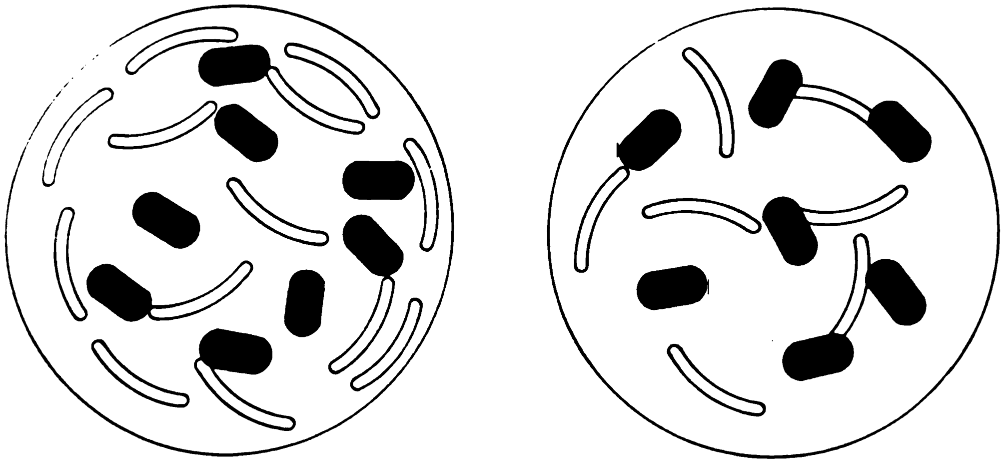
2. Immiscible polymer blend: a blend that is heterogeneous on a macroscopic level. When polymer A forms a separate phase from polymer B, the blend would thus be considered immiscible. Immiscible blends exhibit limited attraction between polymer constituents. The interfaces between the two immiscible species are generally very weak. The overall mechanical properties of the blend

are so poor as to be of little practical utility. The immiscible blend consists of multiple amorphous phases, as shown in Figure 1b. The polymer present in lower concentration usually forms a discontinuous or discrete phase (domain), where as the polymer present in higher concentration forms a continuous phase. The immiscible blends of two polymers show two distinct T_g's which are similar to those of the isolated polymers.

3. Partially miscible polymer blend: a blend of two polymers is neither totally miscible nor totally immiscible, but falls somewhere in between. This type of blend can form complete miscible blends when either polymer is present in small amounts. Phase separation is pronounced as the mixture approaches a 50/50 blend. Where the partially miscible polymer blend is in two phases, the phase may not have a well-defined boundary since polymer A molecules can significantly penetrate into the polymer B phase and vice-versa (see Figure 1c), and often produce an unusually advantageous combination of properties [6]. The molecular mixing that occurs at the interface of a partially miscible two-phase blend can stabilize the domains and improve interfacial adhesion, which, in turn, explains why these two-phase blends generally have good bulk properties. It also shows two T_g's which normally fall between those of the individual polymers. The T_g of the higher component is lowered, whereas that of the lower T_g component is raised because some molecular mixing takes place. Most of the blends that are available in the market are this type of partially miscible blends.



a. Miscible Blend



b. Immiscible blend

c. Partially miscible blend

Figure 1: Miscible, Partially Miscible, And Immiscible Polymer Blends On A Microscopic Scale [10]

Thermodynamics Of Polymer-Polymer Miscibility

From a thermodynamic point of view, every polymer has some solubility in every other polymer, but the magnitude in most cases is exceedingly low. The rules governing miscible behavior of polymer blends are best understood in a thermodynamic context through the Gibbs Free Energy of mixing. In order for two polymers to be miscible, the Gibbs free energy of mixing must be negative. The equilibrium-phase behavior of mixtures is governed by the free energy of mixing [3]

$$G_{mix} = H_{mix} - T(S^{(c)}_{mix} + S^{(e)}_{mix})$$

Where G_{mix} is Gibbs free energy of mixing

H_{mix} is enthalpic which is primarily dependent on the energy change associated with nearest neighbor contacts during mixing and to an approximation is independent of molecular weight.

$S^{(c)}_{mix}$ is the combinatorial entropy of mixing

$S^{(e)}_{mix}$ is the excess entropy of mixing

$S^{(c)}_{mix}$ and $S^{(e)}_{mix}$ are dependent on molecular weight

From the Flory-Huggins equation [3]:

$$\Delta S^{(c)}_{mix} = -R \left[\frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 \right]$$

where V_i is the molar volume of species i and ϕ_i is volume fraction in the blend. V_i is proportional to molecular weight and density. Commercial polymers have high molecular weight. The higher the molecular weight, the higher V_i. From the Flory-Huggins equation, V_i is very high when compared with ϕ_i, therefore, $\Delta S^{(c)}_{mix}$ for polymer mixtures is virtually zero. Because of very small $\Delta S^{(c)}_{mix}$, the $S^{(e)}_{mix}$ may play an important role in overall thermodynamic behavior. $\Delta S^{(e)}_{mix}$ is associated with volume change of mixing which is generally small. Since both $S^{(c)}_{mix}$ and $S^{(e)}_{mix}$ tend to be zero, in order to get a negative value of G_{mix}, H_{mix} must be less than zero.

$$\Delta H_m = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2$$

Where δ_i is the solubility parameter of the pure component [3].

This equation always predicts a positive enthalpy of mixing or at best zero when $\delta_1 = \delta_2$ for mixtures of non-polar material.

The conceptual key toward finding miscible polymer binaries is to choose polymer pairs with chemical structures capable of specific interactions of the type leading to exothermic or negative heats of mixing.

LDPE and LLDPE have similar chemical structure. They are both non-polar materials. When blended together, dispersive interactions between weakly interacting non-polar materials lend to positive heats of mixing, and positive Gibbs Free Energy.

Mechanical Properties

Predicting the mechanical properties of polymer blends is a difficult task. Variations in mechanical properties may be attributable to differences in the number of phases, size of domains, degree of dispersion, and interfacial adhesion. Frequently, the mechanical properties of a polymer blend can be approximated from those components. However, the properties dependent on composition also vary in a complex way with the particular property, the nature of the components (glass, or semicrystalline), thermodynamic state of the blend (miscible or immiscible), and its mechanical state (whether its molecules and phases are oriented by the shaping of the material for testing).

The properties of miscible polymer blends are functions of composition and to some extent the degree of interaction between the blend components. The immiscible polymer blend's properties will depend on the phase morphology and phase interaction as well as composition.

The typical mechanical properties vs compositional plots are step, maximum, minimum, or linear (see Figure 2). The step-shaped plot has been commonly observed for heterogeneous phase or immiscible polymer blends. A maximum is commonly observed for miscible polymer blends because the specific interactions or intermolecular forces (such as hydrogen bonding, van der Waals forces, or dipole moments) that provide miscibility enhance the packing efficiency of the molecules. It has been reported that the mechanical properties of PPO/PS (polyethylene oxide and polystyrene) [9] miscible material is found to be nearly linear. It has been reported as well [9] that the partially miscible blend of PC/PETG (polycarbonate and polyethylene terephthalate glycol monomer) shows a nearly linear relationship. A minimum relationship as a function of composition is reported for the partially miscible blend of PC/acrylic rubber-acrylonitrile-styrene [9].

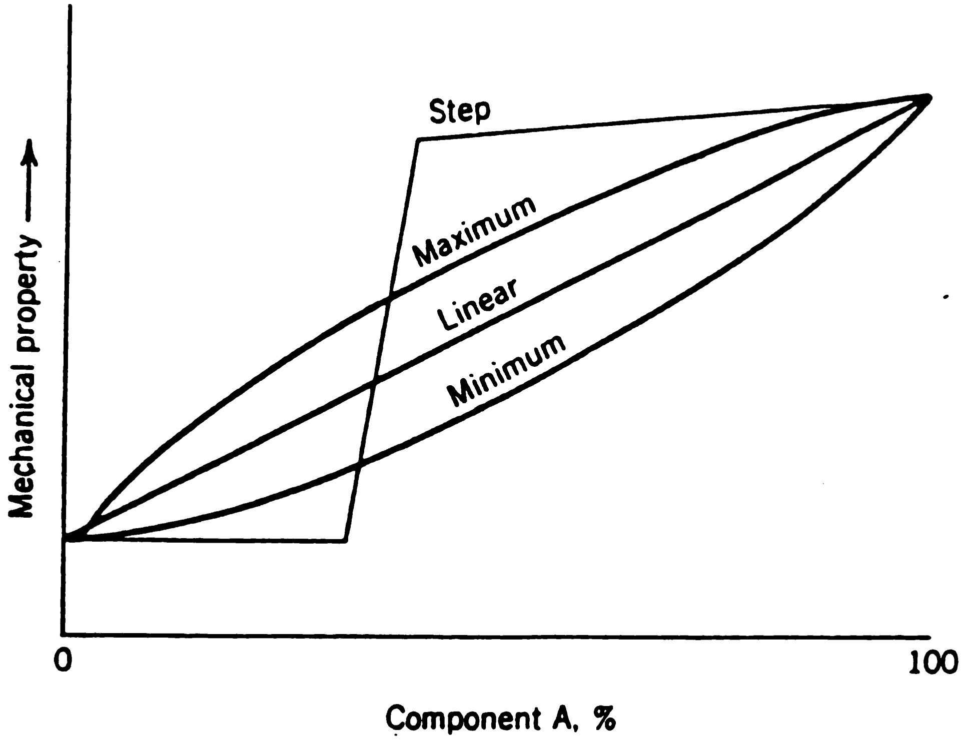


Figure 2: Possible Functions Of Mechanical Properties Vs Two-Component Composition [7]

Beyond the minimal level of thermodynamic compatibility, greater attractive forces between constituents serve to enhance the resultant property profile. In general, two component polymer mixtures may be described by the following relationship [7]:

$$P = P_1C_1 + P_2C_2 + IP_1P_2$$

Where P is the property value of the blend

P_1 and P_2 are the property values of the isolate polymer constituent

C_1 and C_2 are the concentrations of the two polymer components

I describes the level of synergism, or thermodynamic compatibility of the components in the mixture

If it has a positive value, the polymer exhibits a superior property to the weighted arithmetic average of the constituent polymer properties and is termed synergistic. If $I = 0$, the property of the resulting blend is equal to the weighted arithmetic average of the constituent properties. In this case, an additive blend results. If it has a negative value, with properties below those predicted by the weighted arithmetic property averages of the components, a nonsynergistic blend results.

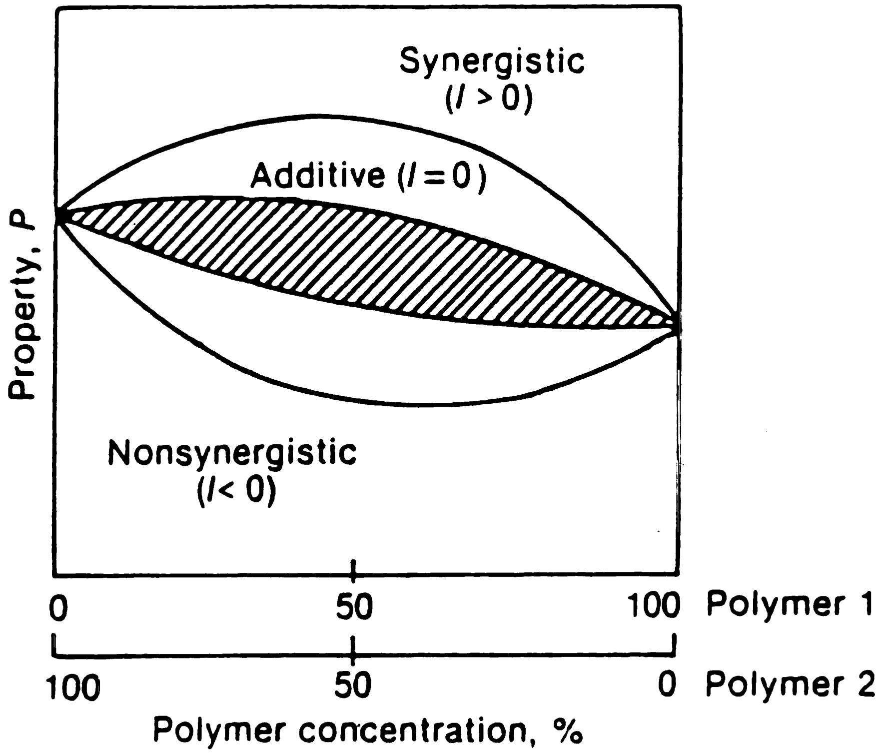


Figure 3: Homogeneity On A Macroscopic Level And A Property Profile Exhibited By Blends [10]

Compatibility Agents

It is possible to enhance the properties and stability of an immiscible polymer blend. Compatibilizing agents are those that have two distinct chemical segments, for example, block or grafted polymers. Compatibilizing agents are added to reduce the tendency of the polymers to separate and improve the interfacial adhesion between phases.

The A-B block copolymer is assumed to selectively dissolve block A in polymer A and block B in polymer B, binding the two A and B phases, ultimately resulting in chemical bonds between the two phases. This method can be utilized only when the compatibilizer polymer segments are identical in chemical composition to the components of the polymer blend.

An immiscible blend can also be enhanced by modification of one or both of the polymers to be blended. This is generally done by grafting a functional group on one polymer, to interact with the other polymer.

2.4 Previous Studies of LDPE/LLDPE Blends

Recently, blends of various polyolefins have been widely studied, for instance, the blends of LDPE/HDPE, HDPE/LLDPE, HDPE/PP, NMWLPE/HMWLPE [12]. However, the studies of the blends between LDPE and linear LLDPE are quite few. Such blends have been studied with a view to improve mechanical properties like impact strength, tensile strength, and processability or rheological properties [1-3,5,13-19]. The previous studies on rheological properties of such blends showed evidence for improvement in processability with increase in LDPE content since the viscosity of the melt is found to decrease with increase in LDPE content [1]. It has been reported that the blend containing about 25% of LLDPE is the most interesting in view of the substituting of the LDPE in the production of film by film blowing since it shows a similar shear viscosity at the rate usually found in production [2,14].

LLDPE exhibits considerably higher tear resistance, impact strength, elastic modulus, and elongation than does LDPE of similar density [18]. Such mechanical properties of LDPE/LLDPE blend are always intermediate between those of the parent polymers [1,13-14] indicating partially miscible behavior [13-14]. Tensile strength and elastic modulus are strongly influenced by the LDPE when LLDPE content is less than 25% [1,14]. The mechanical properties are somewhat related to percent crystallinity. Increase in crystallinity generally increases tensile strength and elastic modulus, but decreases impact strength and percent elongation [6].

Heat-sealing of PE film is sensitive to crystallinity. High crystallinity produces a higher and sharper melting point and thus narrows the range of useful heat-sealability. Seal strength normally depends on the degree of molecular entanglement achieved at the interface. Increase in crystallinity causes decrease in degree of molecular entanglement at the interface. Consequently the lower crystallinity polymer, LDPE, favors easier heat-sealability [6]. Thermal analysis shows a single broad melt peak for LDPE, but a higher and sharper multi peak endotherm for LLDPE of similar density [18].

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

The five blends between recycled LDPE and virgin LLDPE samples used in the present study were provided by Petoskey Plastics Company. The composition of the film samples, expressed as percent (weight/weight) recycled LDPE was as follows: 0%, 10%, 20%, 30%, and 50% respectively.

Each sample was produced by the extrusion blown film process. After the tube passed through the pull rolls, it was sealed to form bags. Each bag was 2-side sealed and was open at the top. The thickness of one side of a bag was approximately 1 mil.

3.2 Methods

The methods used for the mechanical properties study included low strain rate test (tensile properties), and high strain rate tests (free-falling dart impact strength, and Elmendorf tear resistance). The tensile properties, and tear strength were measured in both the machine (MD) and cross direction (CD). The differential Scanning Calorimeter (DSC) was used to characterize the structure of the films, and to determine the crystalline melt temperature of the blend components.

3.2.1 Seal Strength Test

Seal Strength tests were conducted on an Instron Model 4201 Tensile Tester, according to ASTM F 88-85. The type of seal failures were determined by rupture or delamination of seals. Ten specimens were used in each test. The test specimens were randomly cut along the seal of bags. The size of a test specimen was 1" X 6" (excluding the seal width). The Instron Tensile Tester was set to the following conditions:

- The initial gage length was 2 inches.
- The jaw separation rate was 20 in./min.

The data of interest is the type of failure and the maximum force required to cause seal failure which can be directly read from the chart recorder.

3.2.2 Tensile Properties

Tensile property tests were conducted on an Instron Model 4201 Tensile tester, according to ASTM D 882 - 83. The type of failures were determined by rupture of test specimen. Ten specimens were used in each test of each blend sample. The tests were performed in both machine and cross directions. Test specimens were randomly cut from the bags. The size of a test specimen was 1" X 8". The film thickness of each test specimen was measured 5 times, and the average thickness was used in the calculation of tensile properties. The machine and test conditions used were the same as used in the seal strength test. The load, extension, and type of failure from each test were recorded. The tensile properties, tensile strength, percent elongation, and modulus of elasticity were calculated.

3.2.3 Impact Strength

The impact resistance test was conducted on a Free-Falling Dart Impact Tester, according to ASTM D 1709, Method A, staircase method. At least twenty test specimens of each sample blend were used in each test. The test specimens were randomly cut. The size of the test specimen was 7" X 7.5". The C-clamp was used to hold the test specimen in place. The failure was determined by a tear or a hole in the test specimen. The initial dart weight was recorded, and used to calculate impact failure weight.

3.2.4 Tear Resistance

Tearing resistance tests were conducted on an Elmendorf Tearing Tester, according to TAPPI T 414 om - 82. This method determines the average force perpendicular to the plane of the plastic required to tear a single sheet of plastic through a specified distance after the tear has been started using an Elmendorf-type tearing tester. Ten test specimens randomly cut at both machine and cross film directions from the bags of each sample blends were used in each test. The test specimen size was 2.5" X 5". Failure of a test specimen was determined when the pendulum broke through the specimen. The scale reading from each test was recorded, and used to calculate the tearing force.

3.2.5 Differential Scanning Calorimetry (DSC) Thermal Analysis

The crystalline melt temperatures were determined by Differential Scanning Calorimetry thermal analysis on Du Pont Instrument 910 DSC Mode 9900. Two test specimens were prepared from each blend sample. Each specimen was cut into small pieces; 7 to 8 mg. of sample was measured and filled in a bottom pan. A lid was placed on the bottom pan, and compressed closed. The DSC was set to the following conditions:

- Sampling interval was 1.00 second.
- Rate of scanning was 5.00°C/min. to 200°C

Two test specimens were prepared from each blend. Each test specimen was scanned twice. The melt profiles from each scan were obtained from the plotter attached to the DSC. The crystalline melt temperatures of each blend component were determined.

3.3 Statistical Analysis

A major interest of this study was to determine the effect of % recycled LDPE used as a substitute for virgin LLDPE. This was done by determining the % recycled LDPE that could blend into virgin LLDPE without sacrificing the original mechanical properties of LLDPE.

The data was statistically analyzed by MSTAT-C (Microcomputer Program For The Design, Management, and Analysis Of Agronomic Research Experiments). First the data was analyzed by an F-test to see if there was a significant difference in each mechanical property between each sample blend. The Tukey's Honestly Significant Test was later used to determine which level of LDPE in the blend caused the differences in each mechanical property.

CHAPTER IV

DATA ANALYSIS AND INTERPRETATION

In this chapter all the test results are presented in tables. Each mechanical property is reported, analyzed, and interpreted separately. The following parameters are determined: the highest to the lowest level of % recycled LDPE that could be added as a substitute for virgin LLDPE, crystalline melt temperature, and the phase behavior of the blend.

4.1 Seal Strength Test

Table 2: Load Force Applied to Cause Seal Failure in Seal Strength Test and Tukey's Honestly Significant Difference Test Result at 95% Confidence Level

Sample no.	%LDPE added	Average load (lbs.)	Standard deviation	Tukey's Test Result
1	50	2.898	0.45	A
2	30	2.842	0.33	A
3	20	2.880	0.39	A
4	10	2.305	0.17	B
5	0	2.303	0.21	B

The seal strength of the virgin LLDPE was improved by the addition of some recycled LDPE, but over 20% LDPE, there was no significant improvement

The result from the F-Test (see Appendix A) indicates that there is a significant difference in forces applied to cause seal failure between each blend. Tukey's Honesty Significant Difference Test indicates that addition of 10% recycled LDPE as a substitute for virgin LLDPE did not show a significant increase in seal strength. The samples of 0%, 10% recycled LDPE show a significant difference in seal strength from those of 20%, 30%, and 50% recycled LDPE. No significant difference was observed among samples of 20%, 30% , and 50% recycled LDPE content.

Generally LDPE is a easier heat-sealability material compared to LLDPE. Heat sealing of PE film is sensitive to crystallinity. From the DSC melt profiles (see Figure 14-18), LLDPE which is a more highly crystalline material than LDPE produced higher and sharper melting point and thus narrow the range of useful heat sealing tempertures. Consequently lower crystallinity favors easier heat-sealing. LDPE also gives a better seal strength than LLDPE. Seal strength normally depends on how well the molecules entanglement at the interface is achieved. LDPE has more amorphous regions when compared to LLDPE. Therefore, as the LDPE content in the blend increases, the amorphous regions in the blend increases as well. When there exists higher amorphous region in the blend, more molecules entanglement at the interface can be achieved when heat sealing, and higher seal strength results.

No certain relationship (maximum, linear, or minimum) between % recycled LDPE and seal strength was observed. In particular for the seal strength the LDPE exerts a greater influence on this property only for contents of LDPE greater than 10 % (see Table 2). From 20% up to 50% LDPE content there appear to be a slow increase but it was not found to be statistically significant. Therefore, the phase behavior of the blend can not be determined from this test. However, recycled LDPE can be added up to 50% to achieve higher seal strength than 100% virgin LLDPE.

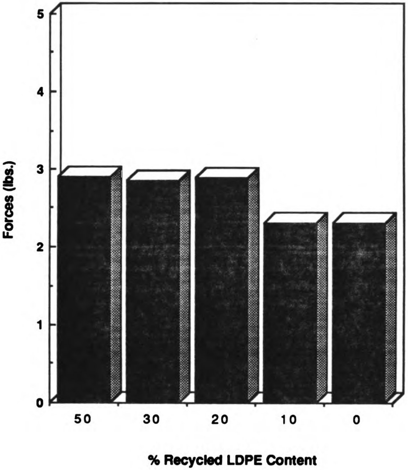


Figure 4: Seal Strength As A Function of % Recycled LDPE

4.2 Mechanical Property Tests

The effect of recycled LDPE added as substitute for virgin LLDPE in blown films on the mechanical behavior at low and high strain rates was investigated. The following properties were calculated: tensile strength, elastic modulus, percent elongation, tearing strength, and impact failure weight.

4.2.1 Tensile Properties Test

Tensile Strength

Table 3: Tensile Strength and Tukey's Honestly Significant Difference Test Result at 95% Confidence Level (Machine Direction)

Sample no.	%LDPE added	Tensile strength at break (psi)	Standard deviation	Tukey's Test Result
1	50	3744.9	355.70	C
2	30	4043.2	303.66	BC
3	20	4322.4	319.49	AB
4	10	4506.3	300.44	A
5	0	4331.7	436.82	AB

Table 4: Tensile Strength and Tukey's Honestly Significant Difference Test Result at 95% Confidence Level (Cross Direction)

Sample no.	%LDPE added	Tensile strength at yield (psi)	Standard deviation	Tukey's Test Result
1	50	2998.9	130.33	A
2	30	3013.7	298.72	A
3	20	3180.3	181.07	A

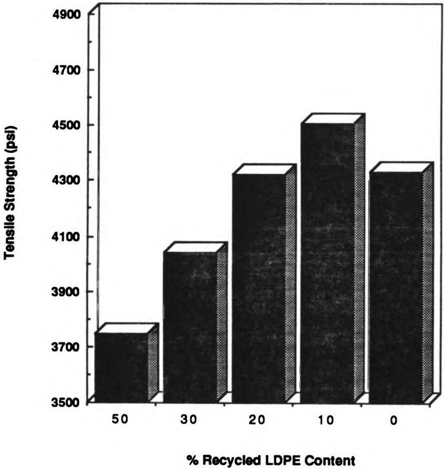


Figure 5: Tensile Strength at Break (Machine Direction)

As A Function of % Recycled LDPE

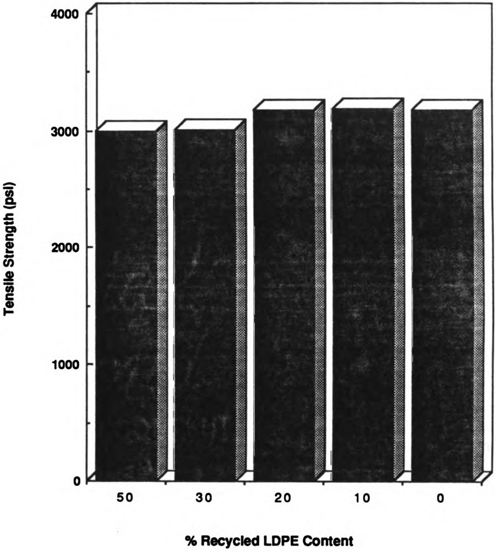


Figure 6: Tensile Strength at Yield (Cross Direction)

As A Function of % Recycled LDPE

Tensile strength is a measure of the maximum load carrying capability of the material. The calculation of this value is in Appendix B. Tensile strength at break was reported in the machine direction because the maximum load was found at break point. Tensile strength at yield was reported in the cross direction because the maximum load was found at the yield point.

F-test results (see Appendix A) show that there is a significant difference between tensile strengths at break, but there is no significant difference between tensile strengths at yield. The addition of 20% LDPE and below decrease the tensile strength at break of virgin LLDPE, but at 30% LDPE, there was no significant decrease. Further analysis, Tukey's Honestly Significant Difference Test, indicates the difference in tensile strength at break to be between the sample of 50% recycled LDPE and the samples of 0%, 10%, and 20% recycled LDPE.

The recycled LDPE has a significant influence on tensile strength only in the machine direction. It can be added as a substitute for virgin LLDPE up to 30% (see table 3) for the blend to still have no significant difference in tensile strength from 100% virgin LLDPE.

No certain relationship between % recycled LDPE and tensile strength in the machine and cross direction was observed. Therefore, phase behavior can not be determined from tensile strength test.

Normally, LLDPE exhibits higher tensile strength than does LDPE (see Table 1). LLDPE has longer main chains or less branches and this makes LLDPE more crystalline than LDPE. The molecules in LLDPE tend to pack into the same lattice. The polymer molecules of the linear structure PE folded back and forth upon itself in a folded lamella type of structure. There exists more tie molecules connecting the lamellae of LLDPE together. Therefore, LLDPE is capable of withstanding more load than LDPE. As mentioned in chapter 2, that the properties of the principle component largely determine the properties of the blend. This explains why when there exists more LLDPE content, the blends exhibit higher tensile strength.

Modulus of elasticity

Table 5: Modulus of Elasticity and Tukey's Honestly Significant Difference Test Result at 95% Confidence Level (Machine Direction)

Sample no.	%LDPE added	Modulus of elasticity (psi)	Standard deviation	Tukey's Test Result
1	50	607.6	39.5	A
2	30	572.7	34.5	A
3	20	602.4	41.9	A
4	10	553.2	109.9	A
5	0	579.6	66.4	A

Table 6: Modulus of Elasticity and Tukey's Honestly Significant Difference Test Result at 95% Confidence Level (Cross Direction)

Sample no.	%LDPE added	Modulus of elasticity (psi)	Standard deviation	Tukey's Test Result
1	50	24440	7717.9	A
2	30	21430	4939.3	A
3	20	22910	3897.3	A
4	10	18400	3310.3	A
5	0	21300	3599.4	A

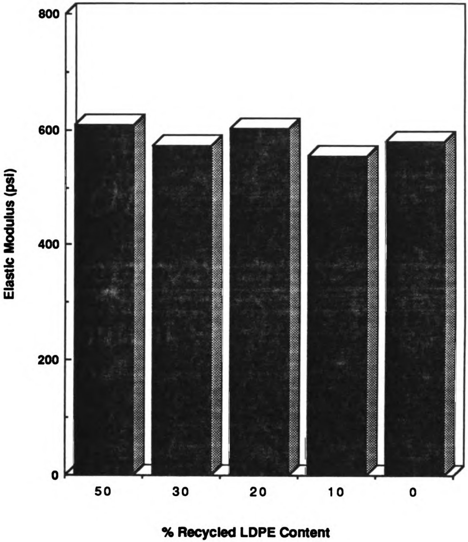


Figure 7: Modulas of Elasticity (Machine Direction)

As a Function of % Recycled LDPE

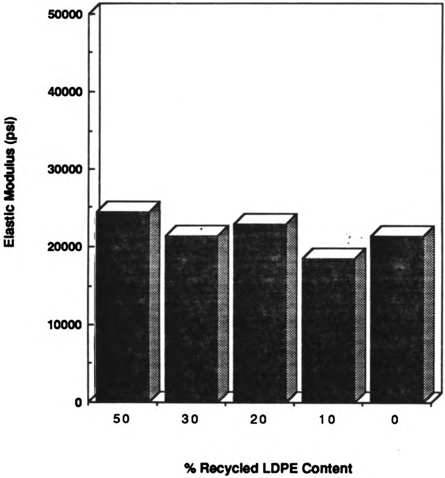


Figure 8: Modulus of Elasticity (Cross Direction)

As A Function of % Recycled LDPE

Modulus of elasticity, alternately referred to as Young's Modulus, can be determined from the ratio of stress to corresponding strain below the proportional limit of a material (see Appendix B). It is a measure of force required to deform the plastic by a given amount and is thus a measure of the intrinsic stiffness of the film.

Normally, LLDPE has almost twice as high a modulus of elasticity as LDPE [11]. It is interesting that addition of LDPE did not significantly decrease this property in the blends. It is possible that addition of recycled LDPE is more sensitive to the change of tensile strength than to the change of modulus of elasticity.

The result from F-test (see Appendix A) shows that there is no significant difference in modulus of elasticity between the blends. The addition of some recycled LDPE did not significantly decrease the modulus of elasticity of virgin LLDPE in either the machine and cross directions. Modulus in a pure polymer, each segment of the polymer molecules has a certain relative freedom to rotate and migrate. When LDPE is added into LLDPE, some polymer molecules of LDPE lie directly adjacent to molecules of LLDPE. Since both LDPE and LLDPE are similar in structure, the ability to rotate and migrate of LLDPE is not restricted by LDPE. The explains why there is no change in modulus of elasticity of the blends no matter how much LDPE is added.

The phase behaviors really cannot be determined at this point because there is no significant difference in this property between each blend. The only conclusion that can be made here is that up to 50% recycled LDPE can be added as a substitute for LLDPE to yield the same modulus properties as does virgin LLDPE.

Percent elongation

Table 7: Percent Elongation and Tukey's Honestly Significant Difference Test Result at 95% Confidence Level (Machine Direction)

Sample no.	%LDPE added	Percent elongation	Standard deviation	Tukey's Test Result
1	50	605.6	97.88	B
2	30	707.4	41.04	AB
3	20	753.4	38.61	A
4	10	764.1	47.42	A
5	0	766.5	43.71	A

Table 8: Percent Elongation and Tukey's Honestly Significant Difference Test Result at 95% Confidence Level (Cross Direction)

Sample no.	%LDPE added	Percent elongation	Standard deviation	Tukey's Test Result
1	50	988.6	28.35	A
2	30	947.4	57.38	A
3	20	983.8	35.31	A
4	10	954.1	63.90	A
5	0	948.4	45.23	A

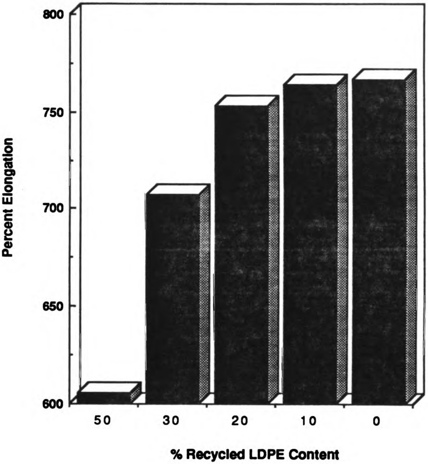


Figure 9: % Elongation at Break (Machine Direction)

As A Function of % Recycled LDPE

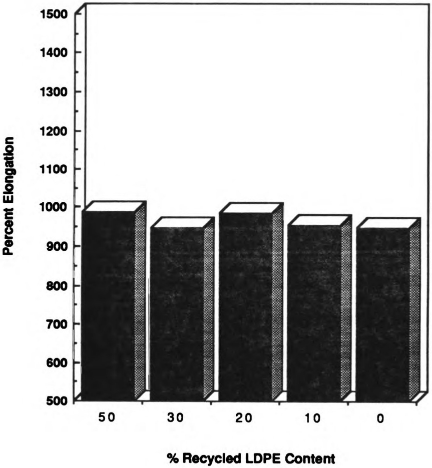


Figure 10: % Elongation at Yield (Cross Direction)
As A Function of % Recycled LDPE

The addition of some recycled LDPE decreases the percent elongation only in machine direction of virgin LLDPE, but below 30% LDPE, there was no significant decrease.

The test results of F-test (see Appendix A) show that there is a significant difference between percent elongation at break of the blends in the machine direction. The Tukey's Honestly Significance Difference Test indicates that the significant different in percent elongation at break of the blends in the machine direction is between the sample of 50% LDPE and the samples of 20%, 10%, and 0% LDPE. There is no significant difference in percent elongation in the machine direction among the sample of 30%, 20% 10%, and 0% LDPE. There is no significant difference between percent elongation at yield in the cross direction.

The percent elongation at break is the percent increase in length produced in the gage length of the test specimen at the moment of rupture of the test specimen. It is a measure of the film's ability to stretch. Elongation represents the extent to which polymer molecules slide pass each other before separating completely at catastrophic failure. It decreases as crystallinity increases. This is due to the decreasing mobility of the system. It has been reported [18] that the spherulitic structure of LLDPE is more regular and consists of larger units relative to that of LDPE. Such structure should result in lower elongation and impact strength. The percent elongation increases when the LLDPE content increases. The increase in crystalline content in the blends does not decrease the percent elongation as it should do.

The increase of percent elongation at break in the machine direction can be explained by structural differences in the amorphous phase. The longer main chains and the narrower length distribution of LLDPE than in the LDPE, having longer branching, results in more tie molecules in the LLDPE than in LDPE. This structure of LLDPE is responsible for the ductility exhibited by LLDPE. Therefore, the increase in percent elongation at break results from the reinforcement effect mainly contributed by the more ductile LLDPE. Recycled LDPE in this case can be added up to 30% to obtain the same value of elongation obtained by 100% virgin LLDPE.

The phase behavior cannot be determined because no significant difference in the cross direction or certain relationship between modulus of elasticity and % recycled LDPE content was found.

4.2.2 Impact Resistance Test

Table 9: Impact Failure Weight Obtained From Impact Resistance Test

Sample no.	%LDPE added	Impact failure weight (lbs.)
1	50	59
2	30	77
3	20	86
4	10	199
5	0	199

The impact failure weight (mass), in this case, is the expressed in terms of the energy that causes 50% failure of the specimens tested. It is a measure of the film's ability to withstand shock loading.

Adding recycled LDPE to the virgin LLDPE was found to decrease impact resistance. Since only one impact failure weight was obtained from each test, therefore, statistical analysis was not employed. From Figure 11 impact failure weight decreases when the percentage of LDPE is decreased from 50% to 10%. In this case the amount of recycled LDPE can be added up to 10% as a substitute for virgin LLDPE without sacrificing the impact strength.

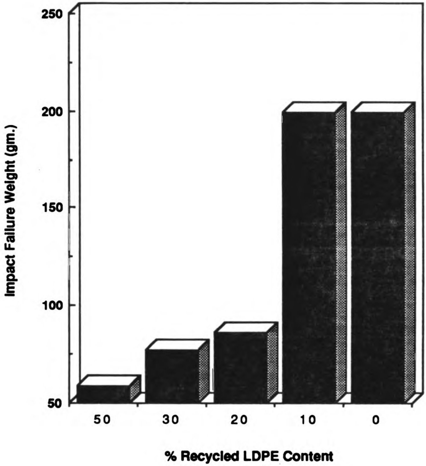


Figure 11: Impact Failure Weight As A Function of % Recycled LDPE

4.2.3 Tear Resistance Test

Table 10: Tearing Force Applied to Cause Failure in Tear Resistance Test and Tukey's Honestly Significant Difference Test Result at 95% Confidence Level (Machine Direction)

Sample no.	%LDPE added	Average tearing force (lbs.)	Standard deviation	Tukey's Test Result
1	50	918.2	328.93	C
2	30	916.6	244.85	C
3	20	1224.3	189.37	C
4	10	1969.8	378.1	B
5	0	2417.2	506.99	A

Table 11: Tearing Force Applied to Cause Failure in Tear Resistance Test and Tukey's Honestly Significant Difference Test Result at 95% Confidence Level (Cross Direction)

Sample no.	%LDPE added	Average tearing force (lbs.)	Standard deviation	Tukey's Test
1	50	7000.4	748.01	B
2	30	8491.5	1017.08	A
3	20	9558.9	1368.75	A
4	10	9149.0	774.93	A
5	0	9150.8	755.66	A

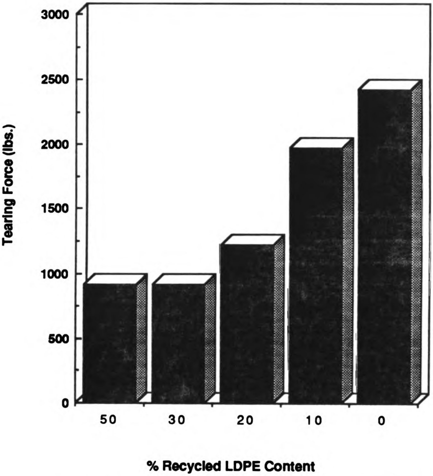


Figure 12: Tearing Force (Machine Direction) As A Function of % Recycled LDPE

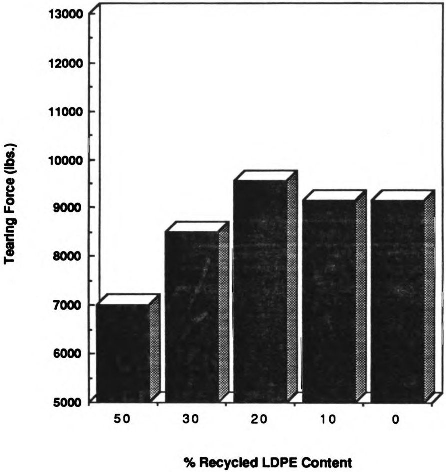


Figure 13: Tearing Force (Cross Direction) As A Function of % Recycled LDPE

The F-test (see Appendix A) results indicate that there is a significant difference in tearing force in both machine and cross directions. Adding 10% of the recycled LDPE reduces the tear resistance in the machine direction of virgin LLDPE. Below 20% LDPE, there is no significant decrease in tearing force in the cross direction. Further analysis for significant difference indicates that the significant difference in tearing force in the machine direction is between the sample of 50% LDPE and the samples of 10%, and 0% LDPE, the sample of 30% LDPE and the samples of 10%, and 0% LDPE, the sample of 20% LDPE and samples of 10%, and 0% LDPE, the sample of 10% LDPE and the sample of 0% LDPE. The is no significant difference in tearing force between the sample of 50% and the sample of 30%, and 20% LDPE. There is a significant difference in tearing force in the cross direction between the sample of 50% LDPE and the samples of 30%, 20%, 10%, and 0% LDPE. There is no significant difference in tearing force among the samples of 30%, 20%, 10%, and 0% LDPE.

Adding 10% recycled LDPE significantly reduced tearing force in the machine direction, while in the cross direction, recycled LDPE can be added up to 30% without reducing the tearing force from that of 100% virgin LLDPE.

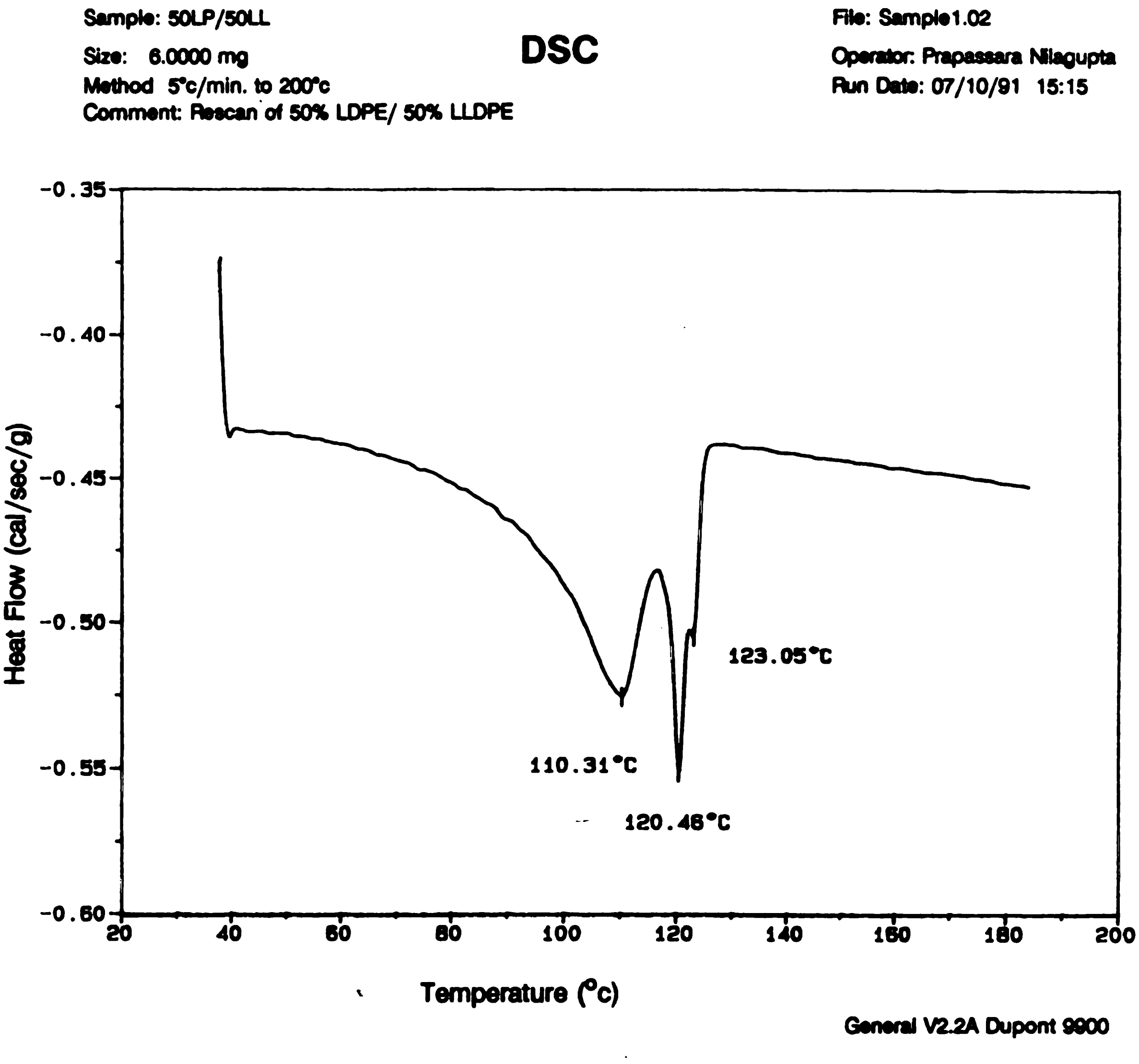
Normally, tear resistance increases when % crystallinity increases [6]. In both the machine and cross directions of the film, tearing force increases when there is more crystalline material, LLDPE, content in the blend. Tearing force in the cross direction is greater than that in machine direction because of the film is oriented in the machine direction.

4.3 Differential Scanning Calorimetry (DSC) Thermal Analysis

Table 12: Crystalline Melt Temperature Obtained From The DSC

Sample no.	% LDPE added	Crystalline melt temperature of LDPE (°c)		Crystalline melt temperature of LLDPE (°c)	
		First scan	Second scan	First scan	Second scan
1	50	-	110.3	-	120.5,123.1[a]
1	50	115.2	110.8	122.9	122.5
2	30	115.2	110.6	122.4	121.7
2	30	115.7	111.1	122.9	122.5
3	20	115.9	110.7	122.7	122.1
3	20	115.5	110.9	122.9	122.9
4	10	116.4	110.8	123.1	122.4
4	10	116.2	111.3	123.0	123.4
5	0	116.1	112.0	112.9	122.5
5	0	116.2	116.2	123.3	122.7

a. Two peaks were observed



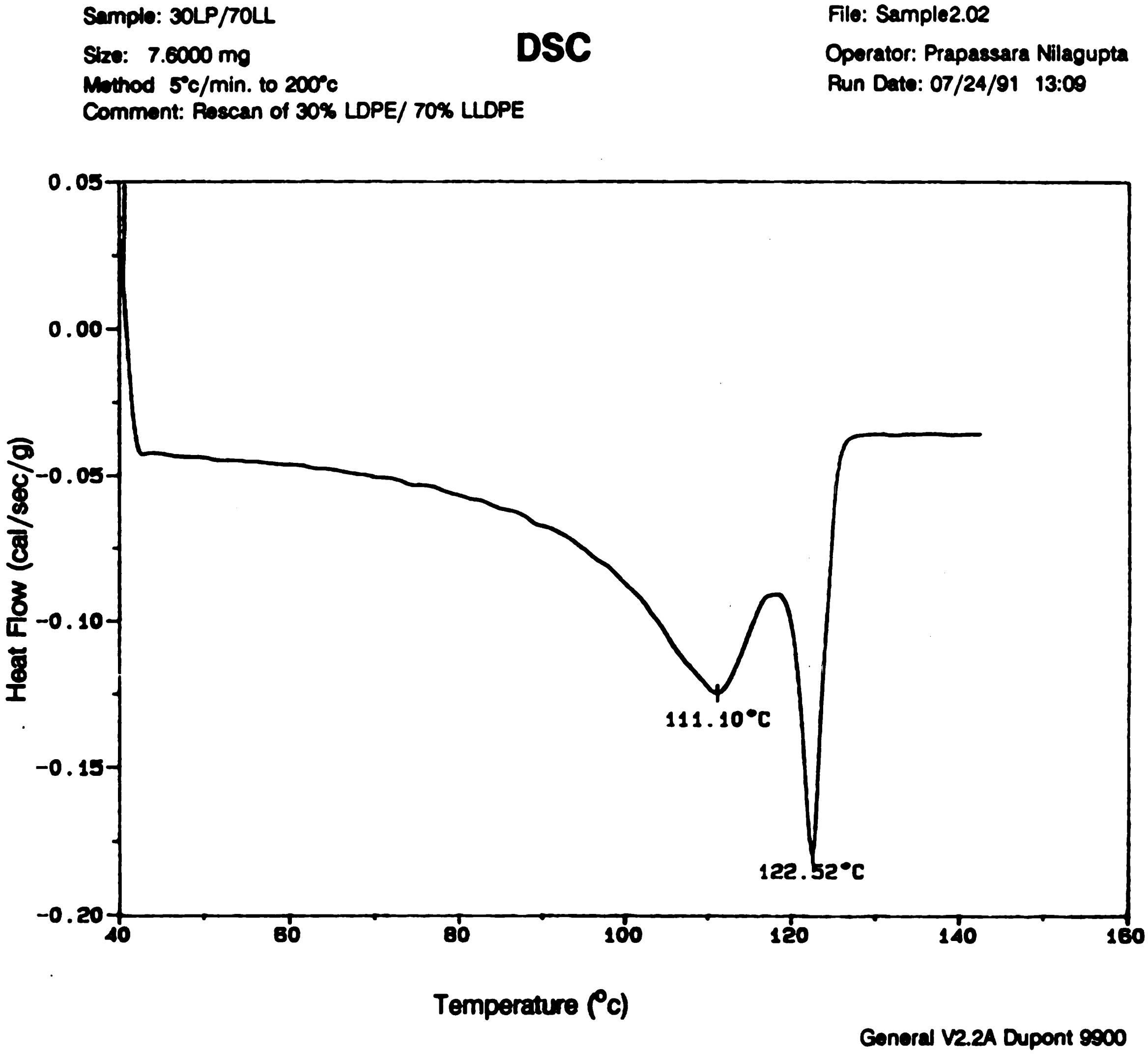
Sample: 50LP/50LL
Size: 6.0000 mg
Method 5°c/min. to 200°c
Comment: Rescan of 50% LDPE/ 50% LLDPE

DSC

File: Sample1.02
Operator: Prapassara Nilagupta
Run Date: 07/10/91 15:15

General V2.2A Dupont 9900

Figure 14: Melt Profile Of 50% LDPE/50% LLDPE From Differential Scanning Calorimetry

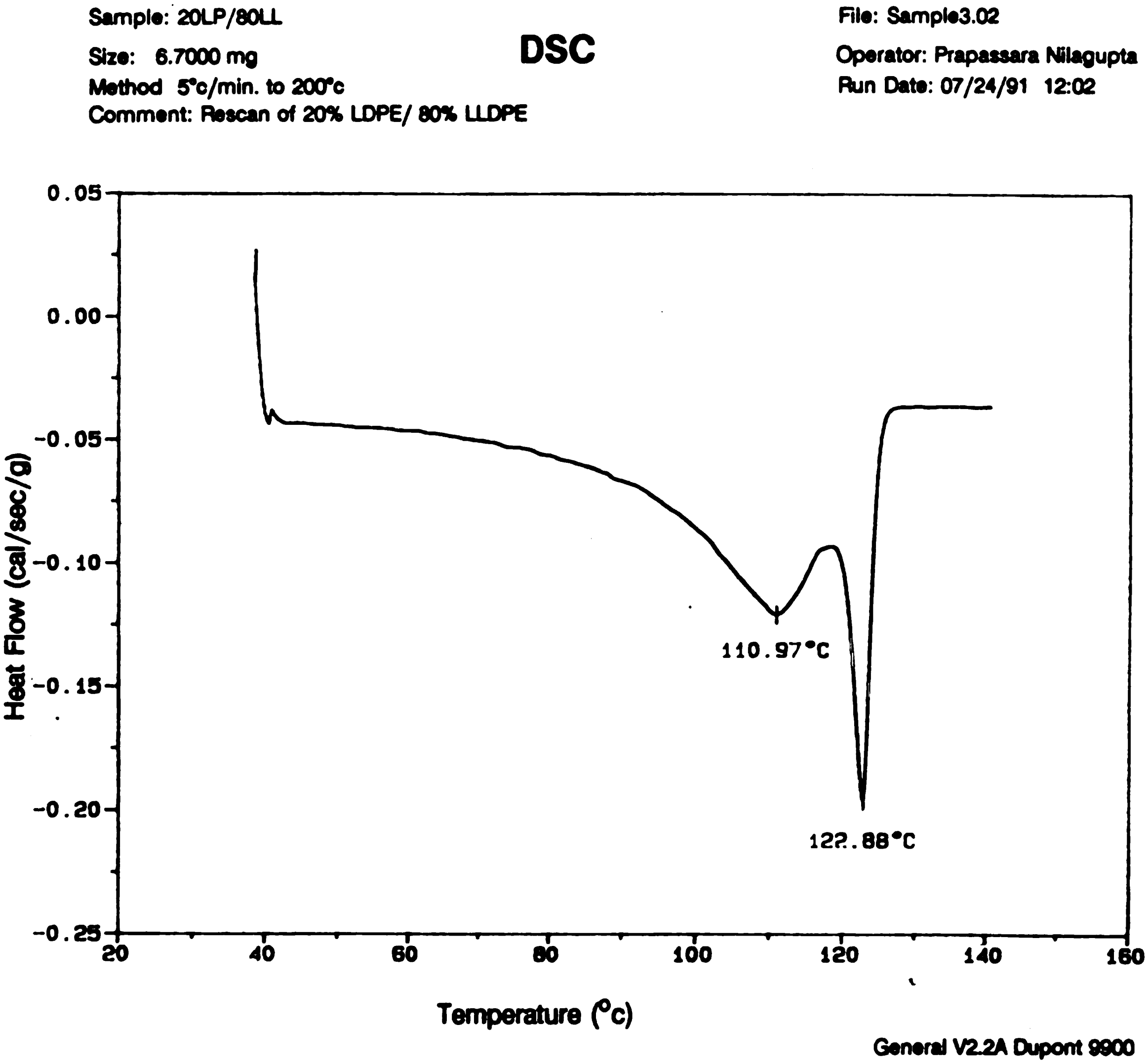


Sample: 30LP/70LL
Size: 7.6000 mg
Method 5°c/min. to 200°c
Comment: Rescan of 30% LDPE/ 70% LLDPE

DSC

File: Sample2.02
Operator: Prapassara Nilagupta
Run Date: 07/24/91 13:09

Figure 15: Melt Profile Of 30% LDPE/ 70% LLDPE From Differential Scanning Calorimetry



Sample: 20LP/80LL
Size: 6.7000 mg
Method 5°c/min. to 200°c
Comment: Rescan of 20% LDPE/ 80% LLDPE

DSC

File: Sample3.02
Operator: Prapassara Nilagupta
Run Date: 07/24/91 12:02

Figure 16: Melt Profile Of 20% LDPE/ 80% LLDPE From Differential Scanning Calorimetry

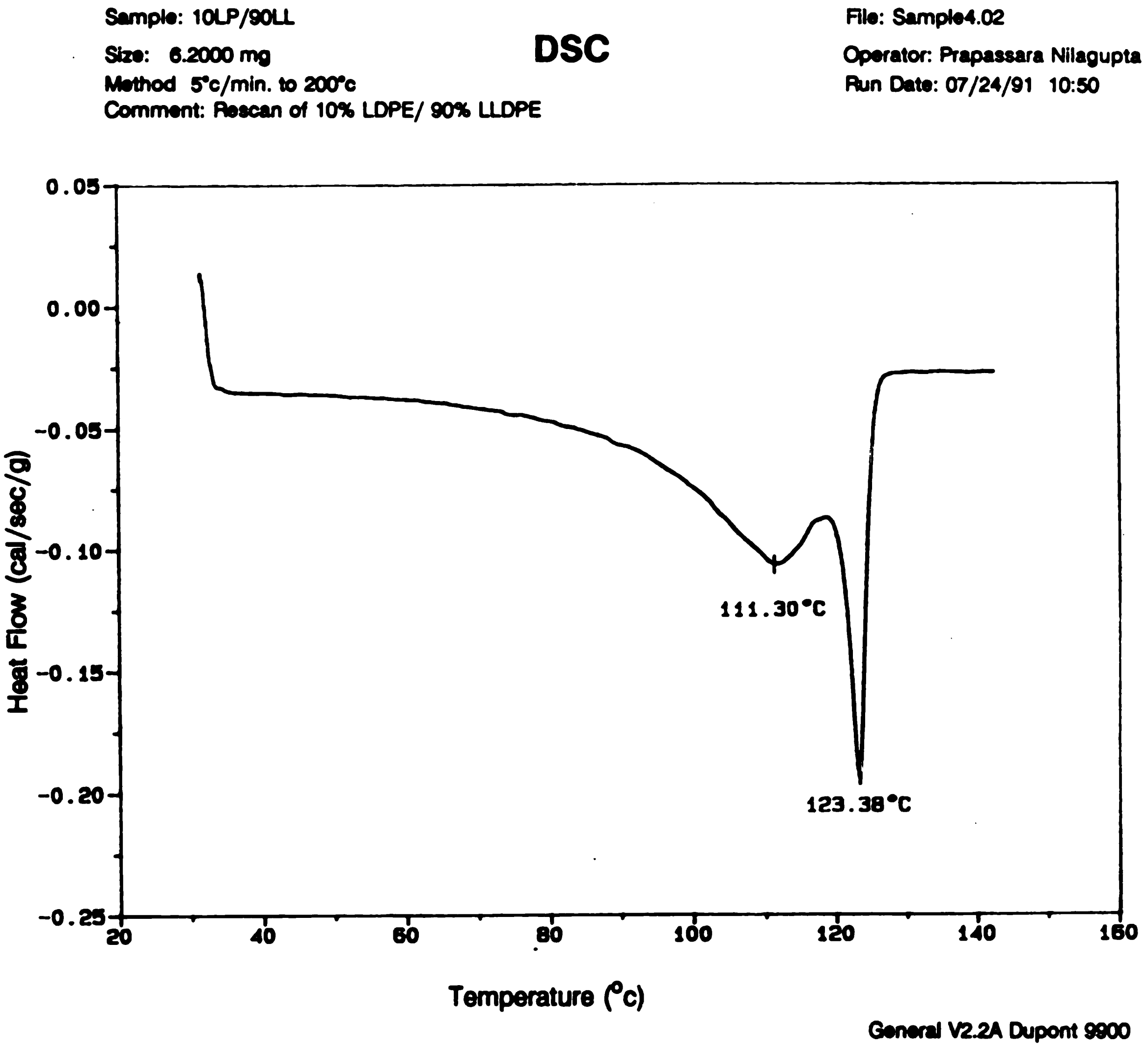
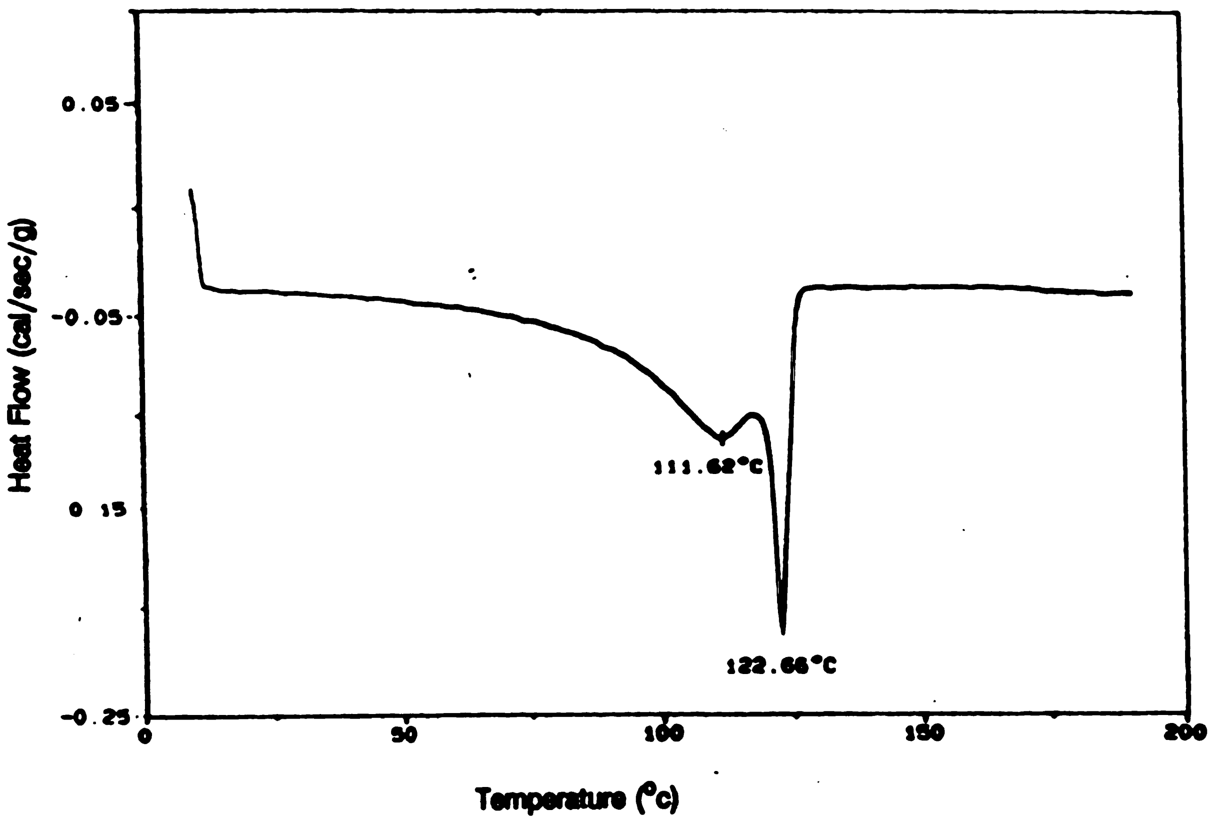


Figure 17: Melt Profile Of 10% LDPE/ 90% LLDPE From Differential Scanning Calorimetry

Sample: 100LL
Size: 6.2000 mg
Method 5°c/min. to 200°c
Comment: Rescan of 100% LLDPE

DSC

File: Sample5.02
Operator: Prapassara Nilagupta
Run Date: 07/24/91 10:50



General V2.2A Dupont 9900

Figure 18: Melt Profile of 100% LLDPE From Differential Scanning Calorimetry

Polyethylene is a semi-crystalline thermo-plastic polymer. Upon the application of heat, it undergoes a process of fusion, or melting, where the crystalline character of the polymer is destroyed. While polymers melt over a temperature range due to differences in the size and regularity of the individual crystallites, the melting point of the polymer is generally reported as a single temperature where the melting of the polymer is complete.

Blending recycled LDPE as a substitute for virgin LLDPE did not change the crystalline melt temperature of virgin LLDPE. At least two crystalline melt temperatures were observed from each blend, indicating that LDPE and LLDPE did not mix at the molecular level.

Interestingly, only the DSC thermogram 50%LDPE/50%LLDPE (see Figure 14) exhibits one crystalline melting peak of LDPE and two crystalline peaks of LLDPE. The rest of the DSC thermograms obtained from 30% LDPE/70% LLDPE (see Figure 15), 20% LDPE/80% LLDPE (see Figure 16), 10% LDPE/90% LLDPE (see Figure 17), exhibit one crystalline melting peak of each component. It should be noted that the DSC thermograms are from the rescan of the specimen after it was cooled (recrystallized). There are several reasons to explain why there is only one crystalline melting peak of LLDPE when there is more LLDPE content in the blends. One explanation is that the temperature difference between 121 and 123 degree celsius is only 2 degrees. It is difficult to detect the difference in morphology of the same material from such a small temperature difference. A second reason is because the rate of scanning is to fast to detect the difference in morphology. The DSC thermogram obtained from 100% LLDPE exhibits two melt temperatures at 116.2°c of LLDPE and at 122.7°c of LLDPE. This indicates that there might be contamination of LDPE in LLDPE during processing.

In all cases, crystalline melting points of LDPE obtained from the first scan are approximately 5 degree celsius more than what are obtained from the second scan. The lower values from second scan indicate less-complete recrystallization under the cooling conditions imposed in the test than was obtained under the original condition. There is no difference in the crystalline melting point of LLDPE obtained from the first and the rescan.

The melt profile of LDPE is much broader than that of LLDPE. This means that LDPE has a broader molecular weight distribution. The low molecular weight molecules melt first, and the highest molecular weight molecules melt last. The molecules of LLDPE have a relatively constant molecular weight. Thus, LLDPE exhibits a nice sharp melting peak. The consequence of the broader melt profile of LDPE is that it allows quite a broad window in which to operate the heat sealing operation. Moreover, the areas under the melt endotherm also indicate the amount of each component in the blend.

Miscible blends show a single, composition-dependent T_g, reflecting the mixed environment of the blend; two phase blends, on the other hand, show two T_g's characteristic of each phase. For miscible systems containing a crystallizable component, a separate crystalline phase of that component can form. In case of LDPE/LLDPE blend, crystallizable polymer component, two crystalline phases were observed, but no certain conclusion associate with phase behavior can be made. The multiple crystalline melt temperatures only tell that there were two separate crystalline phase formed in the blend. The two polyethylenes are different in morphology.

From the results of mechanical and thermal properties of the recycled LDPE/virgin LLDPE blend, the blends tend to exhibit partially miscible behavior. It is not possible that the blend of these two polymer will exhibit miscible behavior, because both LDPE and LLDPE have no chemical structure capable of interacting in specific ways to cause an exothermic heat of mixing. They are thermodynamically immiscible, because both polymers are nonpolar polymers. Nonpolar polymers are generally more attracted to themselves than to other polymers, assuming H_{mix} is usually positive. Therefore, Gibbs free energy of mixing turns out to be positive. But since LLDPE and LDPE are chemically compatible, they can at least exhibit partially miscible behavior.

4.4 Research Limitations

1. It is the glass transition temperature, not the crystalline melt temperature that determines the phase behavior of polymer blends. Instead of determining the crystalline melting point, the glass

transition temperature should have been determined.

2. The deviation of the crystalline melting point of the same blend might result from the method of cooling a test specimen and machine. Most of the rescans of each test specimen were done after the temperature in both machine and test specimen went down to ambient temperature, or not too much above the ambient temperature. The cooling process was mostly done by using water, but there were several times that the cooling process was done by using liquid nitrogen. Cooling by liquid nitrogen made the temperature go down a lot faster than by water. The difference in rate of cooling down the system might make the polymer co-crystalline and has some effect on the deviation of crystalline melt temperature.

3. Measurements were made only of blends of 0 to 50% LDPE, not the whole range of 0 to 100%. It is not therefore, totally correct to conclude the phase behavior of the blend from the tendency of the data obtained from the blend of 0 to 50% LDPE component.

CONCLUSIONS

The following conclusions are based on the data collected from the blends of 0% to 50% recycled LDPE only. These conclusions should not be applied to the blends of 0% to 100% recycled LDPE.

1. The tensile strength, percent elongation, impact resistance, and tearing force of polymer blends tend to reflect a composition weighted average of the properties possessed by LDPE and LLDPE.
2. Recycled LDPE improves seal strength in concentrations above 10%, but over 20% there was no further significant improvement.
3. Tensile strength of the blends is more influenced by LLDPE. Recycled LDPE can be added up to 30% as a substitute for virgin LLDPE without reducing tensile strength from virgin LLDPE.
4. Recycled LDPE added as a substitute for virgin LLDPE has no effect on modulus of elasticity up to 50% LDPE.
5. Recycled LDPE can be added up to 30% as a substitute for LLDPE without reducing percent elongation from virgin LLDPE.
6. Recycled LDPE added as a substitute for virgin LLDPE reduces the impact resistance of virgin LLDPE.
7. Adding 10% recycled LDPE decreases the tearing force in the machine direction.
8. Recycled LDPE can be added as a substitute for virgin LLDPE up to 30% to yield no difference in tearing force in the cross direction.
9. Recycled LDPE added as a substitute for virgin LLDPE did not change T_m of virgin LLDPE.
10. The phase behavior of LDPE/LLDPE blends cannot be determined from this study.

Further Experimental Recommendations

The determination of phase behavior of polymer blends cannot be made accurately from the data obtained from the range of 0% to 50% LDPE in the blends. What should be done is to vary the % LDPE (from 0% to 100%) or % LLDPE (from 100% to 0%) in the blend. In this way, the tendency of the relationship between each mechanical property and the component could be observed in a broader range of data. The phase behavior can as well be determined by the glass transition temperature of the polymer blends.

For polymer blends in which both components are crystalline or semi-crystalline polymers, the percent crystallinity of polymer blends plays an important role on the mechanical properties of the blends. Since both LDPE and LLDPE are semi-crystalline polymers, it is interesting to study the percent crystallinity of the polymer blends between these two components. The percent crystallinity of the blends can also be used to explain the mechanical behavior of the polymer blends. The glass transition temperature and the percent crystallinity of polymer blends can be simply done by Differential Scanning Calorimetry. For more accurant determination of crystalline melt temperature, the rate of scanning should be slower in order to get nicer peaks. It is recommended to change the scanning rate from 5 degree celsius per minute to 2 degree celsius per minute.

This study only investigated the potential of recycling scrap LDPE as a substitute for virgin LLDPE as a polymer blend. Comparing the mechanical properties of such polymers as coextrusion film with those of the blend is also interesting to study.

The LDPE used in this study is clean scrap. Re-use of clean and unmixed plastic scrap is not too complex to do. But a mixture of LDPE and LLDPE often occurs in plastic waste, and the opportunity to commingle them affects the possibility of recycling such low cost material. Although it is expected that post-consumer blends would perform similarily, it is recommended to study the effect of post-consumer recycled LDPE/LLDPE blends.

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APPENDIX A

Analysis of Variance of The Mechanical Properties of LDPE/LLDPE Blend

Table 13: Analysis of Variance Table at 95% Confidence Level for Forces to Cause Seal Failure

Source of Variation	Degree of Freedom	Sum of Squares	Mean	F-values	Prob.
Between	4	0.445	1.114	10.245	0.000
Within	45	4.892	0.109		
Total	49	9.346			

Table 14: Analysis of Variance Table at 95% Confidence Level for Tensile Strength at Break (Machine Direction)

Source of Variation	Degree of Freedom	Sum of Squares	Mean	F-values	Prob.
Between	4	3573423.1	893355.8	7.421	0.0001
Within	45	5416889.6	120375.3		
Total	49	8990312.9			

Table 15: Analysis of Variance Table at 95% Confidence Level for Tensile Strength at Yield (Cross Direction)

Source of Variation	Degree of Freedom	Sum of Squares	Mean	F-values	Prob.
Between	4	365350.3	91337.6	1.197	0.3251
Within	45	3433232.3	76294.1		
Total	49	3798582.6			

Table 16: Analysis of Variance Table at 95% Confidence Level for Modulus of Elasticity (Machine Direction)

Source of Variation	Degree of Freedom	Sum of Squares	Mean	F-values	Prob.
Between	4	19890.3	4972.6	1.184	0.331
Within	45	188911.7	4198.04		
Total	49	208802.1			

Table 17: Analysis of Variance Table at 95% Confidence Level for Modulus of Elasticity (Cross Direction)

Source of Variation	Degree of Freedom	Sum of Squares	Mean	F-values	Prob.
Between	4	200676690	50169172	2.038	0.105
Within	45	1107591869	24613153		
Total	49	1308268558			

Table 18: Analysis of Variance Table at 95% Confidence Level for % Elongation at Break (Machine Direction)

Source of Variation	Degree of Freedom	Sum of Squares	Mean	F-values	Prob.
Between	4	184626.3	46156.6	13.644	0.000
Within	45	152228.5	3382.9		
Total	49	336854.8			

Table 19: Analysis of Variance Table at 95% Confidence Level for % Elongation at Yield (Cross Direction)

Source of Variation	Degree of Freedom	Sum of Squares	Mean	F-values	Prob.
Between	4	16164.9	4041.2	1.761	0.1534
Within	45	103252.2	2294.5		
Total	49	119417.1			

Table 20: Analysis of Variance Table at 95% Confidence Level for Tear Resistance Test (Machine Direction)

Source of Variation	Degree of Freedom	Sum of Squares	Mean	F-values	Prob.
Between	4	18161845.3	4540461.3	37.6	0.0000
Within	45	5436067.6	120801.5		
Total	49	23597912.9			

Table 21: Analysis of Variance Table at 95% Confidence Level for Tear Resistance Test (Cross Direction)

Source of Variation	Degree of Freedom	Sum of Squares	Mean	F-values	Prob.
Between	4	40699874.7	10174968.7	10.9	0.0000
Within	45	41750840.5	927796.5		
Total	49	82450715.2			

APPENDIX B

Calculations of Mechanical Properties

Calculation of Tensile Properties

1. Tensile Strength: the maximum tensile stress sustained by the specimen during a tension test.

$$\text{Tensile Strength} = \frac{\text{Maximum load}}{\text{Minimum Cross Section Area}}$$

2. %Elongation: the increase in length produced in the gage length of the test specimen by a tensile load

$$\%\text{Elongation} = \frac{\text{Extension}}{\text{Original Gauge Length}}$$

3. Proportional Limit: the greatest stress which a material is caable of sustaining without any deviation from proportionality of stress to strain (hooke's law.

4. Modulus of Elasticity: the ratio of stress to corresponding strain below the proportional limit of a material.

$$\text{Modulus of Elasticity} = \frac{\text{Stress}}{\text{Strain}}$$

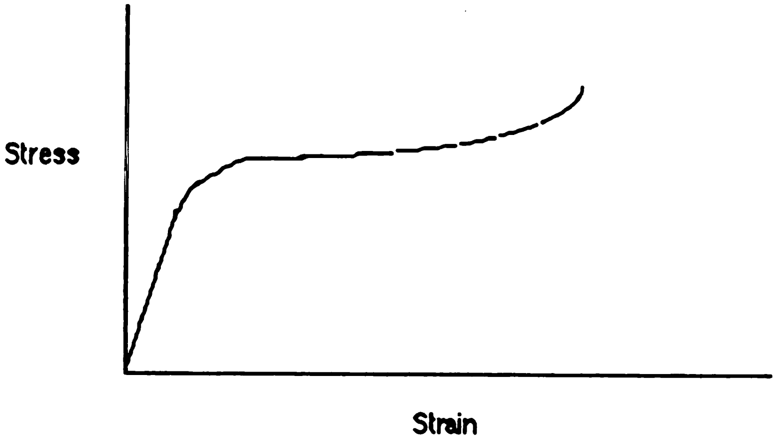

Figure 19: Normal Stress and Strain Curve

Calculation of Impact Failure Weight

$$W_f = W_o + [\ W(A/N - 1/2)]$$

where W_f is an impact failure weight

n_i is the total number of X's at each missile weight

i is 0 to n where 0 is for the lowest missile weight at which n_i value has been entered

A is the product of in_i

W_o is a missile weight to which an n_i value zero is assigned

ΔW is the uniform missile weight employed

N is total number of failures

Calculation of Tearing force

$$\text{Average tearing force, gf.} = \frac{16 \text{ X average scale reading}}{\text{number of piles}}$$

APPENDIX C

Raw Data

Table 22: Load and Extension Obtained from Seal Strength Test of Sample No. 1

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	3.119	5.868	delamination
2	2.679	5.412	delamination
3	3.925	12.800	break at seal
4	2.556	3.500	delamination
5	3.162	7.339	break at seal
6	2.642	4.886	break at seal
7	2.405	4.005	break at seal
8	3.173	9.176	break at seal
9	2.776	6.651	break at seal
10	2.561	5.774	break at seal

Table 23: Load and Extension Obtained from Seal Strength Test of Sample No. 2

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	2.545	4.191	delamination
2	3.248	9.985	break at seal
3	2.774	6.932	break at seal
4	3.189	10.330	break at seal
5	3.039	9.192	break at seal
6	2.330	3.030	delamination
7	2.459	5.012	break at seal
8	2.878	6.818	break at seal
9	2.985	8.221	break at seal
10	2.706	7.318	break at seal

Table 24: Load and Extension Obtained from Seal Strength Test of Sample No.

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	3.495	14.120	break at seal
2	3.098	12.050	break at seal
3	3.425	12.500	break at seal
4	3.323	12.040	break at seal
5	2.663	9.972	break at seal
6	2.421	4.316	delamination
7	2.507	7.918	break at seal
8	2.642	10.240	break at seal
9	3.184	11.990	break at seal
10	3.039	11.380	break at seal

Table 25: Load and Extension Obtained from Seal Strength Test of Sample No. 4

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	2.298	10.500	break at seal
2	2.089	5.521	delamination
3	2.507	9.355	break at seal
4	2.250	9.387	break at seal
5	2.454	9.994	break at seal
6	2.352	7.877	break at seal
7	2.475	10.220	break at seal
8	2.368	6.334	break at seal
9	1.976	5.295	break at seal
10	2.260	7.634	break at seal

Table 26: Load and Extension Obtained from Seal Strength Test of Sample No. 5

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	2.110	9.624	break at seal
2	2.846	11.880	break at seal
3	2.341	7.544	break at seal
4	2.250	10.700	break at seal
5	2.405	10.540	break at seal
6	2.174	9.534	break at seal
7	2.196	10.060	break at seal
8	2.309	10.700	break at seal
9	2.266	10.520	break at seal
10	2.153	10.200	break at seal

Table 27: Load and Extension Obtained from Tensile Properties Test of Sample No.1

(Machine Direction)

Replication	Load (lbs.)	Extension	Type of Failure
1	4.225	14.23	break at upper jaw
2	4.011	14.11	break at lower jaw
3	3.715	13.35	break at upper jaw
4	4.113	13.60	break at upper jaw
5	3.318	9.756	break at middle jaw
6	3.871	13.12	break at lower jaw
7	3.248	11.18	break at upper jaw
8	3.898	12.89	break at upper jaw
9	3.060	9.38	break at lower jaw
10	3.071	9.51	break at lower jaw

Table 28: Load and Extension Obtained from Tensile Properties Test of Sample No.1 (Cross Direction)

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	3.447	20.63	break at upper jaw
2	3.334	20.02	break at upper jaw
3	3.216	19.53	break at lower jaw
4	3.173	19.58	break at lower jaw
5	3.404	20.11	break at upper jaw
6	2.985	19.86	break at lower jaw
7	2.862	19.54	break at lower jaw
8	2.695	18.46	break at lower jaw
9	3.093	20.04	break at upper jaw
10	3.039	19.95	break at upper jaw

Table 29: Load and Extension Obtained from Tensile Properties Test of Sample No.2 (Machine direction)

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	4.182	14.90	break at upper jaw
2	5.170	15.49	break at lower jaw
3	4.059	14.50	break at upper jaw
4	4.213	14.66	break at upper jaw
5	3.737	13.27	break at upper jaw
6	3.946	14.17	break at upper jaw
7	3.893	13.21	break at upper jaw
8	4.016	14.38	break at upper jaw
9	3.474	12.89	break at upper jaw
10	3.876	14.00	break at upper jaw

Table 30: Load and Extension Obtained from Tensile Properties Test of Sample No.2 (Cross Direction)

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	2.706	17.13	break at lower jaw
2	3.157	18.91	break at upper jaw
3	3.662	20.59	break at upper jaw
4	3.544	20.10	break at upper jaw
5	2.787	17.86	break at upper jaw
6	2.819	18.79	break at lower jaw
7	3.119	19.75	break at upper jaw
8	2.921	18.55	break at lower jaw
9	2.668	17.78	break at lower jaw
10	3.544	20.02	break at upper jaw

Table 31: Load and Extension Obtained from Tensile Properties Test of Sample No.3 (Machine Direction)

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	3.721	13.66	break at lower jaw
2	4.424	14.78	break at upper jaw
3	4.166	15.17	break at upper jaw
4	5.219	15.72	break at upper jaw
5	5.177	16.38	break at upper jaw
6	4.703	14.45	break at upper jaw
7	4.682	14.75	break at lower jaw
8	4.166	14.69	break at lower jaw
9	4.644	15.19	break at upper jaw
10	4.440	15.37	break at lower jaw

Table 32: Load and Extension Obtained from Tensil Properties Test of Sample No.3 (Ccross Direction)

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	3.758	20.48	break at lower jaw
2	3.383	20.04	break at upper jaw
3	3.302	20.18	break at lower jaw
4	3.168	19.25	break at upper jaw
5	2.894	18.05	break at lower jaw
6	3.801	20.11	break at upper jaw
7	3.297	19.53	break at lower jaw
8	3.699	20.14	break at lower jaw
9	3.447	19.24	break at lower jaw
10	3.468	19.73	break at upper jaw

Table 33: Load and Extension Obtained from Tensile Properties Test of Sample No.4 (Machine Direction)

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	4.381	15.63	break at upper jaw
2	5.638	16.49	break at lower jaw
3	4.478	14.93	break at upper jaw
4	4.795	16.38	break at upper jaw
5	4.344	13.82	break at lower jaw
6	4.413	15.26	break at lower jaw
7	5.068	15.99	break at lower jaw
8	5.154	15.58	break at lower jaw
9	3.565	1.374	break at upper jaw
10	4.199	15.00	break at lower jaw

Table 34: Load and Extension Obtained from Tensile Properties Test of Sample No.4 (Cross Direction)

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	3.301	20.27	break at lower jaw
2	4.054	20.47	break at lower jaw
3	3.066	18.77	break at lower jaw
4	3.624	19.11	break at lower jaw
5	3.318	18.66	break at upper jaw
6	3.007	18.37	break at upper jaw
7	3.817	20.68	break at lower jaw
8	2.647	16.25	break at lower jaw
9	3.205	19.08	break at lower jaw
10	3.195	19.15	break at upper jaw

Table 35: Load and Extension Obtained from Tensile Properties Test of Sample No. 5 (Mmachine Direction)

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	5.638	16.10	break at lower jaw
2	4.027	15.25	break at upper jaw
3	3.961	14.42	break at upper jaw
4	4.923	16.72	break at upper jaw
5	4.698	15.76	break at lower jaw
6	4.800	15.40	break at upper jaw
7	4.521	15.26	break at lower jaw
8	5.326	16.19	break at upper jaw
9	3.726	13.92	break at upper jaw
10	3.887	14.48	break at upper jaw

Table 36: Load and Extension Obtained from Tensile Properties Test of Sample No.5 (Ccross Direction)

Replication	Load (lbs.)	Extension (in.)	Type of Failure
1	3.227	17.99	break at upper jaw
2	3.447	18.70	break at lower jaw
3	4.321	20.28	break at lower jaw
4	3.834	19.55	break at lower jaw
5	3.603	19.47	break at upper jaw
6	3.640	19.21	break at lower jaw
7	3.699	19.00	break at lower jaw
8	3.424	18.53	break at upper jaw
9	3.522	19.75	break at lower jaw
10	3.039	17.19	break at upper jaw

Table 37: Scale Reading Value from A Tear Resistance Test of Sample no. 1

Replication	Scale reading value	
	machine direction	cross direction
1	3.5	49.5
2	6.0	49.5
3	8.5	40.5
4	6.0	39.5
5	6.0	39.5
6	3.5	38.6
7	4.0	46.5
8	6.0	44.0
9	10.0	48.0
10	5.0	50.5

Table 38: Scale Reading Value from A Tear Resistance Test of Sample No. 2

Replication	Scale reading value	
	machine direction	cross direction
1	4.5	58.5
2	5.0	63.0
3	7.0	58.0
4	6.0	56.5
5	6.5	42.0
6	7.0	46.0
7	5.5	53.5
8	8.9	50.0
9	4.0	59.5
10	4.0	54.0

Table 39: Scale Reading Value from A Tear Resistance Test of Sample No. 3

Replication	Scale reading value	
	machine direction	cross direction
1	7.0	54.0
2	9.0	54.0
3	7.5	67.0
4	6.5	75.5
5	10.5	53.5
6	7.5	49.0
7	7.5	64.0
8	8.5	71.0
9	7.0	65.5
10	7.0	56.0

Table 40: Scale Reading Value from A Tear Resistance Test of Sample No. 4

Replication	Scale reading value machine direction	 cross direction
1	16.0	59.0
2	12.0	63.5
3	8.5	54.0
4	13.5	54.0
5	13.5	61.5
6	9.0	68.0
7	14.0	59.5
8	11.0	65.5
9	13.5	53.0
10	14.5	54.0

Table 41: Scale Reading Value from A Tear Resistance Test of Sample No. 5

Replication	Scale reading value machine direction	 cross direction
1	18.0	53.0
2	10.5	57.0
3	15.5	53.5
4	14.0	52.0
5	16.0	62.5
6	21.5	64.0
7	17.5	56.0
8	16.0	65.0
9	11.5	61.5
10	13.5	59.0

Table 42: The Result Fom Impact Resistance

Sample no.	N	A	W_o	W	W_f
1	10	2	63.76	15	59.26
2	10	14	63.76	15	77.26
3	10	16	63.76	15	80.26
4	10	12	108.76	15	119.26
5	10	12	108.76	15	119.26

Table 43: Calculated Tensile Properties Values from Tensile Properties Tests (Machine Direction)

Sample no.	Replication	Tensile Strength (psi)	%Elongation	Modulus of elasticity
1	1	4225.0	711.1	13333
1	2	4011.0	705.5	20000
1	3	4127.8	667.5	14583
1	4	3808.3	680.0	20000
1	5	3160.3	487.8	23000
1	6	3910.1	656.0	15000
1	7	3608.9	559.0	16667
1	8	3859.4	644.5	22500
1	9	3326.1	468.9	17500
1	10	3412.2	475.7	15000
2	1	3801.8	745.0	20000
2	2	4535.1	774.5	20000
2	3	4018.8	725.0	20000
2	4	4089.1	733.0	26667
2	5	3628.2	663.5	20000
2	6	4026.5	708.5	17500
2	7	3707.6	660.5	21000
2	8	4462.2	719.0	19500
2	9	3903.4	644.5	16000
2	10	4259.3	700.0	16500
3	1	4044.6	683.0	13333
3	2	4253.9	738.0	20000
3	3	4124.8	785.5	25000
3	4	4349.2	786.0	25000
3	5	4968.0	819.0	17500
3	6	3964.3	768.5	17500
3	7	4036.2	737.5	20000
3	8	4479.6	734.5	16000
3	9	4300.0	759.5	25000
3	10	4703.0	722.5	25000

Table 43: (Cont'd)

Sample no.	Replication	Tensile Strength (psi)	%Elongation	Modulus of elasticity
4	1	4867.8	781.5	12500
4	2	4860.4	824.5	21000
4	3	4390.2	746.5	14000
4	4	4447.5	819.0	15000
4	5	4344.0	691.0	23333
4	6	4369.3	763.0	19500
4	7	4862.7	799.5	20000
4	8	4295.0	779.0	25000
4	9	3961.1	687.0	13500
4	10	4665.6	750.0	14000
5	1	5125.5	805.1	13333
5	2	3909.7	762.6	18000
5	3	3883.3	721.1	16500
5	4	4558.3	836.1	11250
5	5	4474.3	778.1	11667
5	6	4247.8	770.0	17500
5	7	4521.0	763.0	12500
5	8	4787.4	809.5	18500
5	9	3802.0	696.0	20000
5	10	4007.2	724.0	23000

Table 44: Calculated Tensile Properties Values from Tensile Properties Tests (Cross Direction)

Sample no.	Replication	Tensile Strength (psi)	%Elongaton	Modulus of elasticity
1	1	3162.4	1031.3	20000
1	2	3030.9	1001.0	22875
1	3	3005.6	976.5	25000
1	4	2911.0	976.0	40000
1	5	3066.7	1005.5	35000
1	6	3021.6	977.0	17500
1	7	2722.2	923.0	16500
1	8	3172.3	1002.0	25000
1	9	2979.4	997.5	17500
1	10	2926.5	993.0	25000

Table 44: (Cont'd)

Sample no.	Replication	Tensile Strength (psi)	%Elongaton	Modulus of elasticity
2	1	2529.0	856.5	16000
2	2	2870.0	945.5	23333
2	3	3555.3	1029.5	20000
2	4	3136.3	1005.0	30000
2	5	2732.4	893.0	30000
2	6	3031.2	939.5	17000
2	7	3088.1	987.5	19000
2	8	3042.7	927.5	19000
2	9	2808.4	889.0	19000
2	10	3343.4	1001.0	21000
3	1	3447.7	1024.0	20000
3	2	3161.7	1002.0	20000
3	3	3205.8	1009.0	25000
3	4	3046.2	962.5	20000
3	5	2809.7	902.5	21053
3	6	3110.4	976.5	21000
3	7	3362.7	1007.7	20000
3	8	3113.6	962.0	25000
3	9	3211.0	986.5	32000
3	10	3334.2	1005.5	25000
4	1	3519.4	1013.5	15667
4	2	3652.3	1023.5	23500
4	3	3227.4	938.5	16500
4	4	3179.0	955.5	15000
4	5	3044.0	933.0	13333
4	6	3068.4	918.5	18500
4	7	3470.0	1034.0	22500
4	8	2406.4	812.5	19000
4	9	3052.4	954.0	19000
4	10	3227.3	957.5	21000
5	1	2734.8	899.5	19500
5	2	3379.0	935.0	21000
5	3	3858.0	1014.0	18500
5	4	3363.2	977.5	18000
5	5	3160.5	973.5	19000
5	6	3339.5	960.5	23000
5	7	2802.3	950.0	20000
5	8	3112.7	926.5	30000
5	9	3291.6	984.5	24000
5	10	2737.84	859.5	20000