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PHOTODEGRADATION OF CROP TRELLISING PLASTIC TWINE

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MARIA-PAZ GONZALEZ MULET

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Master in Science degree in Packaging

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PHOTODEGRADATION OF CROP TRELLISING PLASTIC TWINE

By

Maria-Paz González Mulet

A THESIS

Submitted to
Michigan State University
In partial fulfillment of the requirements
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ABSTRACT

PHOTODEGRADATION OF CROP TRELLISING PLASTIC TWINE

By

Maria Paz González Mulet

In Guatemala, snow peas and broccoli share the same field and are planted in alternating cycles. Snow peas are a creeping plant and need to have support on a number of lines that actually are currently made from black polypropylene twine. After some time, when the twine photodegrades, hair-shaped twine fragments get entangled in the growing heads of the broccoli. When the growers want to pack the broccoli they have to remove all these filaments because they are considered a contaminant and not allowed in exports. This study aims to find replacement for the existing twine to avoid a packing problem after harvesting.

Experiments were conducted in a QUV apparatus where UV light was produced to simulate photodegradation in the field. Black and white polypropylene twine and four different nylon monofilaments were tested.

Two of the nylon samples performed best and can be considered as a solution for the problem. A field study is recommended to validate the results and correlate the behavior of the twines and monofilaments exposed in the UV apparatus with those exposed outdoors.

Dedication

To Luis, Jorge, Mireille, Marichu and Natalia.

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My husband

My family

My friends

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Chapter 1
Introduction

Between May and August of 2002, a subsector analysis of the frozen vegetable sector in Guatemala was developed by Michigan State University and PFID-F&V (Partnerships for Food Industry Development- Fruits & Vegetables) aiming at the establishment of a sound business strategy for the next several years in the U.S., European and Asian markets. Part of the study included also the identification of key specific problems in the production and distribution chain affecting exports. This research was done to address a specific problem identified in the snow pea and broccoli industry in Guatemala concerning the use of a plastic twine as a trellising material.

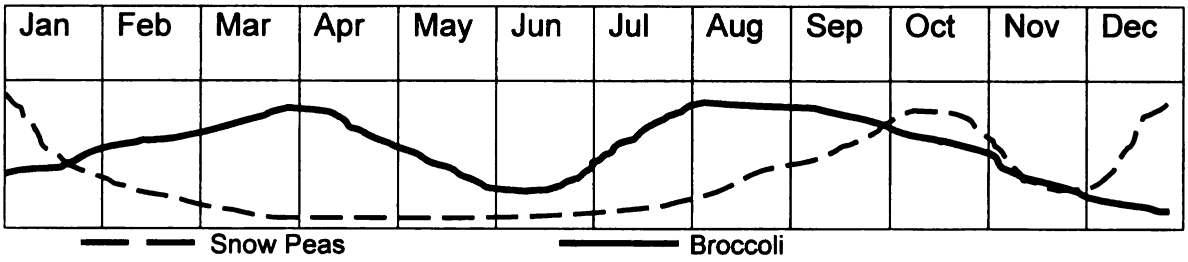
Located south of Mexico, as Figure 1 represents, Guatemala's mountains, valleys and lowlands give the country its own range of climates and great biodiversity. The North Central region along the eastern slopes of the Cuchumatanes Plateau, with its abundant rainfall, cooler climate and ample supply of labor, is the nation's primary snow pea and broccoli production area.

Figure 1. Guatemala Map
Source: Lonely Planet, 2003

Snow peas and broccoli share the same conditions. Therefore, they have the following growing areas (regions) in commons: Quiche, Baja Verapaz, Sácatepequez, Guatemala, Santa Rosa, Sololá, Chimaltenango and Totonicapán (MAGA 2001).

Crop cycling is a recommended practice in agriculture to break down the pest life cycles of a single product and, in the case of Guatemala, to take advantage of different market windows in the export industry. Snow peas and broccoli plantations are cycled on the same land because they need the same cold weather, and requiring temperatures below 80° F. (Ohio State University Extension Fact Sheet 2004), in alternating seasons as is shown in Table 1. Snow peas are harvested from December to January and again in October. Broccoli is harvested in March to April and July through August.

Table 1. Snow peas and broccoli harvest times.
Source: Ministerio de Agricultura de Guatemala, MAGA, 2001



Because snow peas are a vine type plant, they need the help of a trellis of several lines where they can climb and thrive making the product cleaner by avoiding it touching the ground, and also making the harvest easier for farmers. In Figure 2 an image of a snow pea field is shown the use of the twine to hold the plant in a vertical position can be observed.

Figure 2. Snow pea plants
Source: www.floridata.com 2004

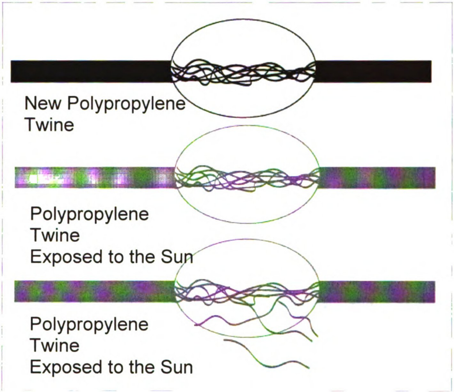
Currently, farmers are using black polypropylene twine, and even when they remove it from the trellising poles between crops, the degraded old twine is left in the fields at the ends of the rows. This means that when snow peas have been harvested, the twine remains in the fields before, during and after the broccoli season. The main reason for not removing the twine between crops is that such activity would be labor intensive, thus increasing production costs forthe grower.

In Contrast to snow peas, broccoli is not a creeping plant and the heads start developing at a very low height, close to the ground where the twine remnants have not been removed. In Figure 3 a broccoli head is shown.

Figure 3. A broccoli head
Source: MAGA 2003

With exposure to the sun, the polypropylene twine will start to degrade, changing color to a faded gray and then cracking. This twine is a multifilament twine in a net type structure with unions at some points. Figure 4 is a representation of the twine and how it degrades.

Figure 4. Representation of the polypropylene twine and the stages of degradation.



When the polypropylene twine used in the field starts to photodegrade under UV light, it looks like loose black human hair. These hair-like fibers find their way to the broccoli heads through wind or rain, and are very hard to remove mechanically at the time of harvesting or when controlling quality prior to export. Finding such material on an edible product is considered by quality and safety inspectors as physical contamination and a threat to human health.

Once in the processing plant, broccoli for export that has these hairs like filaments has to be removed, and the process is labor intensive and costly. It is also not 100% effective. This contamination is highly penalized in the Japanese market, where Guatemala has lost export opportunities to other countries such as Mexico or Ecuador, since these countries do not use the twine in their fields or are capable of removing the traces of the twine in a total and efficient manner. It has been declared by some industry people, that totally removing such fibers would cost each processing plant an increase in payroll due to the need to hire more people for quality control. Such a situation cannot be afforded in a sector that is challenged every day by more efficient competitors, demanding the exporters use cost-reduction methodologies all along the production and supply chain.

Three major objectives for this study are to find a replacement for the polypropylene twine that: (1) must stay in place for two years (2) can degrade in a way other than a hair-shape (3) is cost effective. The price of a pound of snow peas sold by the farmer in bulk is not higher than US $ 0.10. The actual cost of a 10-pound roll of twine in Guatemala is equivalent to $7.48 at the current exchange rate of Q 7.75[1] per U.S. dollar (Banco de Guatemala, January 27, 2003). Rolls are shown in Figure 5.

Figure 5. Polypropylene twine
Source: Olefinas.com 2003

The experiment exposes the polypropylene twine and possible alternatives in the Q-UV light apparatus for a predetermined period. The samples are then tested periodically for tensile strength following the procedures of ASTM Standard D638-02 ("Standard Test Method for Tensile Properties of Plastics")

The materials tested are the black polypropylene twine with carbon black as a UV stabilizer, currently used in Guatemala; a white polypropylene twine with titanium as a UV stabilizer; and 30 pounds test nylon monofilaments.

White twine was considered I this study as a possible alternative to black twine based on the following hypothesis: (1) Black color absorbs more UV-Light than white color that refracts more light. (2) Black twine will behave differently than white twine because the presence of the carbon black UV stabilizer (Carlson et al 1984). Nylon was selected for proving the last hypothesis, (3) Polypropylene multifilament will degrade differently than nylon monofilament.

This literature review discusses the characteristics of polypropylene, nylon, and the effects of ultraviolet light on polymers.

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[1] Q. Stands for Quetzales, the Guatemala currency.

Chapter 2
Literature Review

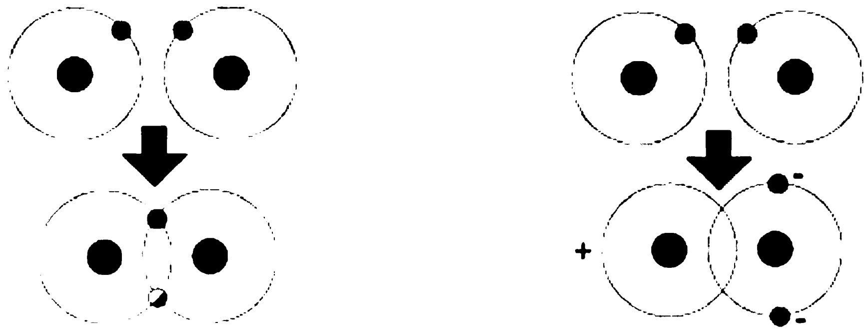
Plastics

Plastics are a specific category of high molecular weight materials that belong to the family of polymers. The first man-made plastic was the cellulose nitrate, which was used in films and was created in 1838. After the Second World War, polyethylene began to be produced in large quantities. As years went by, many other plastics were developed with different properties and were substitute for different uses.

Polymers can be homopolymers, meaning that they made from only one type of monomer, or copolymers, those made from different types of monomers. These can be block, alternating, random or graft. Linear and branched polymers are called thermoplastics; they can be melted and shaped into different forms repeated, using a combination of pressure, heat and time (almost all the packaging plastics are thermoplastics). Thermoset plastics are those plastics with a cross-linked structure.

These are two different types of bonds in the polymer chains: the primary bonds that hold the monomers together shown in Figure 6, which can be covalent bonds or ionic bonds, and the secondary bonds that hold with each other.

Figure 6. Different types of bonds possible in polymers.
Source: Brigdson 1999



Covalent Bond

- **Strongest of chemical bonds**
- Formed by the sharing of a pair of electrons
- Sharing can be equal or **unequal**
- Can be single, double or triple.

IonicBond

- Complete transfer of electrons
- Results in one positive ion and one negative ion

Secondary bonds are weaker than primary bonds, and solids experience the strongest secondary bonds. Dispersion secondary bonds are the weakest, induction secondary bonds are of medium strength, and the strongest are dipole bonds. UV light will start by disrupting the weaker bonds. (Rodriguez 1996)

There are six different things that can affect the physical properties of a polymer. (1) The type of monomer making up the polymer chains of the plastic. , (2) the average chain length (3) the distribution of the molecular weight, (4) the type of chains, (5) the arrangement of the chains and (6) additives that will affect the other five and enhance different properties (Brigdson 1999).

The morphology of a polymer refers to the shape, the arrangement and the physical state of the molecules. This will define how crystalline or amorphous is a polymer because the polymer molecules tend to move towards an arrangement that is the lowest energy state possible, and that will define a crystal form. Crystallinity is obtained when a polymer is capable of packing in a close, regular, predictable and parallel pattern and this will be related to the conformation of the polymer. Many things can interfere with this configuration but the most common will be the presence of chiral carbons that disrupts the symmetry of the molecule.

- Polypropylene

There are two main ways to produce a polymer. The first one is called addition polymerization and is usually based on a free radical reaction. Ones the reaction has been started the molecules start to add one at the time to the growing chain. Polypropylene belongs to this category. Polypropylene is a linear, addition polymer developed by Ziegler, (Germany), Natta (Italy) and Peace and Roedel in the USA in 1950. Cracking petroleum products and fraction distillation of the C_3 produces PP.

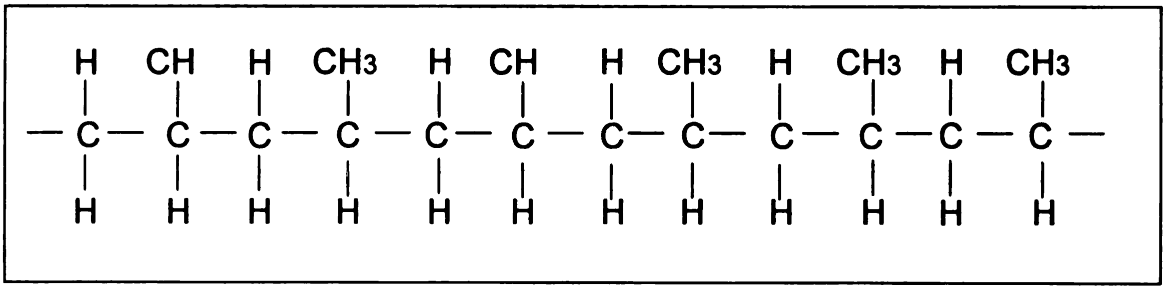
The second broad category is the condensation polymerization where the units are added but they loose one part that is a sub product of the reaction. Generally is water or alcohol. Nylons are part of this last family of polymers. Figure 8 shows the three steps for addition polymerization. The initiation step begins with one molecule called the initiator that breaks into two free radicals, and from there it starts to join to new monomers. The initiators tend to be peroxides (ROO), hydroperoxides (ROOH), azo compounds (-N=N-), ultraviolet light, or heat. The second step is the propagation, when the monomers start to be added to the chain, in the third step, termination something happens and disrupts the chain growth.

Tacticity is the way pendant groups are arranged along the backbone chain of a polymer; for polypropylene the CH_3 groups are those pendant groups. They are three broad categories of tacticity: (1) Isotactic when the pendant groups are always in one side of the molecule chain; (2) Syndiotactic is when the pendant group alternates side of the chain in a regular pattern, and (3) Atactic when there is not a specific pattern in the position of the pendant group in relation to the chain.

Commercial polypropylene tends to be isotactic with a "head to tail" configuration since it has the best properties for general applications. This is used in fibers, films and injection molding. The structure is shown in Figure 7. It is made with a Ziegler-Natta catalyst under controlled temperature and pressure. Syndiotactic polypropylene which can be made with a single site catalyst is less crystalline than isotactic, with less tensile strength and heat resistance and greater susceptibility to solvents. Atactic polypropylene, without a established pattern, is less crystalline than the two mentioned above. Atactic polypropylene is amorphous, soft and rubbery, and is not used much in packaging. (Rodriguez 1996)

Figure 7. Isotactic Polypropylene

Source: Rodriguez 1996

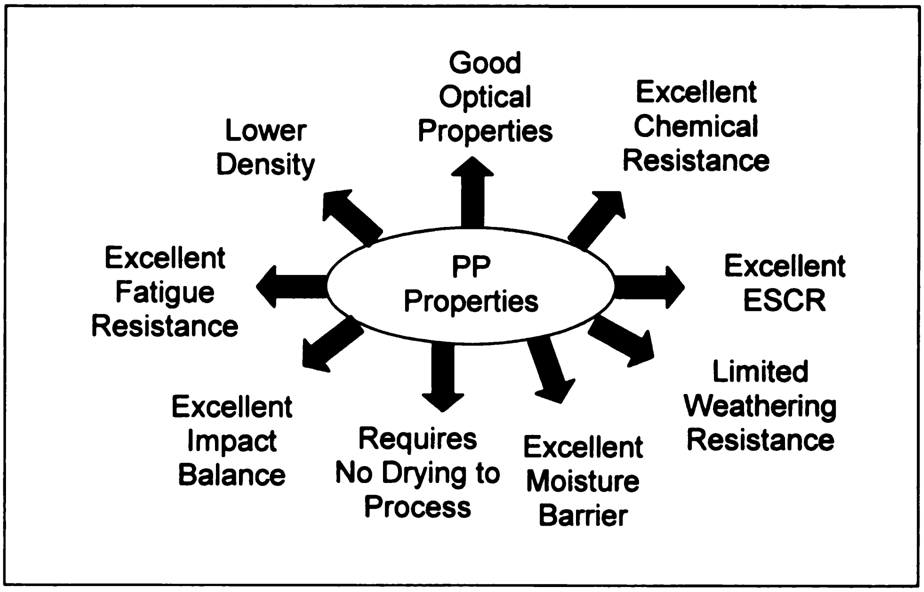


$$\begin{array}{ccccccccccccccccccccccccc}
 & \mathrm{H} & & \mathrm{CH} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{CH} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{CH_3} & \\
 & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & \\
- & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \\
 & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & \\
 & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} &
\end{array}$$

Polypropylene is a linear hydrocarbon polymer, thermoplastic and the major packaging plastic with the lowest density, ranging from 0.90 to 0.96 g/cm^3. It is typically 60% crystalline with a glass transition temperature (Tg) of -10° Celsius, which makes it tend to be brittle at lower temperatures. It is stiffer than polyethylene, a melting point (Tm) of 176° Celsius, high tensile strength and good transparency and gloss. Polypropylene is a low cost polymer and has good chemical resistance. These properties are essential in the twine because the creeping of the plants will be less difficult than on polyethylene, and it will have resistance to fertilizers and pesticides.

Polypropylene is a polymer with a disruption in the crystallinity due to the presence of C_3 in the chain. This disruption increases the crystalline melting point, decreases the crystalline lattice, and increases in the transparency. Polypropylene molecules cannot crystallize in a zigzag pattern like polyethylene but rather in a helix with 3 molecules to complete one loop. Polypropylene can be in a right handed helix or left handed or both. Polypropylene has a density of 0.90 g/cm^3, has a higher softening point, apparently is free from environmental stress cracking, and is more brittle than PE and more susceptible to oxidation. Figure 8 summarizes polypropylene's properties (Bridgson 1999).

Figure 8. The most important properties of PP.
Source: Down Chemical 2003



The presence of the tertiary carbon makes the polymer more susceptible to oxidation and photodegradation. Heat leads to chain scission rather than cross-linking with different consequences that will be discussed later.

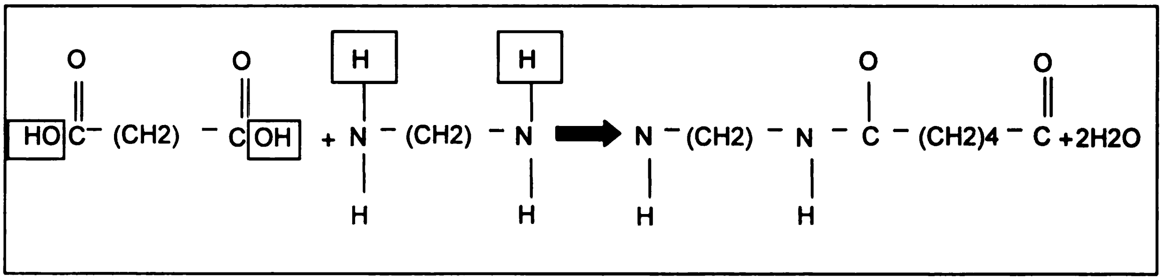
The most important additives in polypropylene are: fillers, rubbers to decrease brittleness, pigments, carbon black as an ultraviolet absorber, antioxidants and nucleating agents. (Brigdson 1999)

- Nylon

The other important category of polymer is the condensation polymers. They have a "step-wise-reaction" normally slower than the addition polymerization reaction. They are normally formed of at least two different monomers but they are not considering being a copolymer. These monomers have to have at least two reactive groups like an alcohol and an amine to produce nylon, or an acid and an alcohol to produce polyester. As part of the condensation reaction, a byproduct is produced, often is water. Polyethylene terephthalate, polyethylene naphthalate, and nylons belong to the same condensation family.

Nylons are also called polyamides; they are thermoplastics with a linear structure. The nomenclature at the end of the name will indicate the size of the amides and acids they are formed from. Figure 9 will show the chemical reaction for producing nylon 6, 6.

Figure 9. Nylon 6, 6 reaction
Source: Rodriguez 1996



$$\boxed{HO}\overset{\overset{O}{\|}}{C}-(CH2)-\overset{\overset{O}{\|}}{C}\boxed{OH}+\underset{\underset{H}{|}}{\overset{\overset{\boxed{H}}{|}}{N}}-(CH2)-\underset{\underset{H}{|}}{\overset{\overset{\boxed{H}}{|}}{N}}\rightarrow\underset{\underset{H}{|}}{N}-(CH2)-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{|}}{C}-(CH2)4-\overset{\overset{O}{\|}}{C}+2H2O$$

The structure of polyamides is crystalline, with a density of $1.14g/cm_3$. Some nylons have an elongation rate of 150% and a tensile strength of 7600 psi. The melting point is 490° F. It is translucent with a good resistance to ultraviolet light and solvents but poor resistance to alkalis and solvents. Also it is a very low weight material but very strong. (Rodriguez 1996)

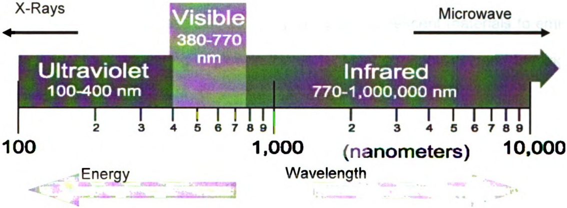
During the course of the experiments and looking for a possible solution for the problem, nylon was chosen because of its properties, the strength and ultraviolet light absorption capacity, and also because it is available in all the Guatemalan markets at an affordable price. The 1000 meter rolls range in price approximately, from Q.10.00 to Q.15.00, equivalent to $1 to 2 US. (Hiper Paiz 2003).

Ultra-violet light and fluorescent lamps

Ultraviolet light (UV light) is part of the light energy spectrum emitted naturally by the sun. The spectrum includes gamma and x-rays, UV light, visible light, infrared rays, microwaves, and radio waves, listed in order of decreasing frequency and increasing wavelength. Figure 10 shows the division of light waves included in UV light. These waves are shorter than visible light; they cannot be detected by the human eye. UV light is invisible, but can cause other substances to glow or fluoresce in a variety of colors visible to the human eye.

Figure 10. Division of the light waves

Source: International Lights 2003



UV light is divided, into four broad categories: short, medium, long, and vacuum wave radiation. Long wave UV has a wavelength of 315 to 400 nanometers and is the less damaging and closer to the visible range. Medium wave has a wavelength of from 280 to 315 nanometers and it is responsible for polymers photodegradation. A nanometer is the unit of length used to define wavelengths in the electromagnetic spectrum, and is equal to one millionth of a millimeter. Table 2 lists the division of UV light.

Table 2: UV light ranges and characteristics.

Source: International Lights 2003

Range Name	Characteristics	Wavelength Range (nm)	Causes for human exposure
UVA	Long waves	315-400	Sun tanning
UVB	Medium waves	280-315	Sun burn and cancer
UVC	Short waves	200-280	Absorbed by DNA producing mutations
Vacuum UV (VUV)	Vacuum UV (VUV)	100-200	Strongly absorbed by water and air and transmitted in vacuum

UV-A is the least harmful and most commonly found type of UV light, because it has the least energy. UV-A light is often called black light, and is used for its relative harmlessness and its ability to cause fluorescent materials to emit visible light - thus appearing to glow in the dark. Most phototherapy and tanning booths use UV-A lamps.

UV-B typically is the most destructive form of UV light, because it has enough energy to damage biological tissues, yet not quite enough to be completely absorbed by the atmosphere. UV-B is known to cause skin burns and cancer. For this experiment UV-B lamps were chose because they are the ones emitting the wavelength that destroys the polymer structure.

Short wavelength UV-C is almost completely absorbed in air within a few hundred meters. When UV-C photons collide with oxygen atoms, the energy exchange causes the formation of ozone. UV-C is almost never observed in nature, since it is absorbed so quickly. Germicidal UV-C lamps are often used to purify air and water, because of their ability to kill bacteria.

Although the sun is the principal source of UV light, it can be reproduced by different kinds of devices like the UV tanning devices that emit the UVA region and are suitable for human exposure. Another important device emitting UV light is the arc welding equipment, which emits very strong levels of UV light due to the excitation of atoms and molecules in the air. Without the correct protection, it can cause burns in the cornea and retina. Arc welding emits UV-B waves in combination with visible light and infrared (Ryer 2003).

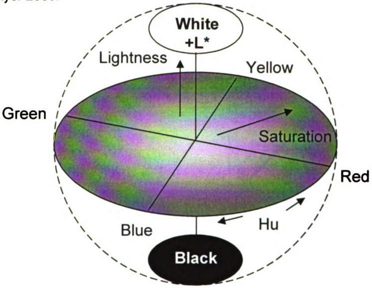
Light absorption, reflection and refraction

Incident light can be reflected, scattered or absorbed by polymers. The first law of photochemistry of Grotthus-Draper said that only the absorbed part of light would lead to photochemical transformation.

Most models of perceived color contain three components: hue, saturation, and lightness. Generally, color is modeled as a sphere, with lightness comprising the linear transform from white to black, and hues modeled as opposing pairs, with saturation being the distance from the lightness axis, as shown in Figure 11 where black and white are opposites in lightness.

Figure 11. Model of colors in a sphere

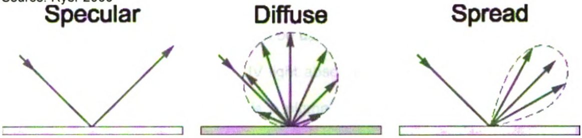
Source: Ryer 2000.



Light can be absorbed, reflected or refracted by a material. It can be reflected by a mirror or by color with a high content of metal particles. Reflection can be spread, diffuse or specular as is shown in Figure 12, where the material is not absorbing light, just redirecting it.

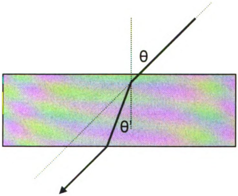
Figure 12. Specular, diffuse and spread reflection from a surface

Source: Ryer 2000



Refraction is when a material absorbs a quantity of light and lets it pass through the material. The rest of the energy is redirected at a different angle. Because a white color is full saturation of light, it refracts more light than black, while black is zero saturation and absorbs all light. Figure 13 shows how refraction works.

Figure 13. Refraction.
Source: Ryer 2000



Absorption of light will depend on the degree of saturation of light of a particular color. Black materials will absorb more light and will get hotter than white materials (South Florida Test Services 1993).

The other important issue about color is that this color can come from a specific additive added to the polymer during processing. In the case of black, the additive is carbon black which can be used as an antioxidant, as an antistatic, as an organic pigment and as a UV light absorber. White is commonly created by adding titanium dioxide which is a pigment but does not have the UV light stabilizer properties. Other colorless stabilizers can be added, but the cost of production will increase. Carbon black is the least expensive of the additives (Gatcher & Müller 1985).

Polymer Degradation

Processes involving chain polymerization, addition, or condensation reactions are used to manufacture most commercial plastics, such as polypropylene. These processes are generally controlled to produce individual polymer molecules with a defined average molecular weight (or molecular weight distribution), degree of branching, and composition that will determine the specific characteristics of each polymer.

During this process or by further exposure to heat, light, air, water, radiation or mechanical loading, chemical reactions will tend to produce modifications in the polymer chain resulting in a change in molecular composition and molecular weight due to chain scission and cross linking, and the specific characteristics of each polymer will tend to change. The stability of a polymer can be affected by its own chemical makeup, its processing history and parameters, and the additives and contaminants present in the polymer. This is why the presence of the CH_3 group in the polypropylene molecule will make it more susceptible for oxidation and photo degradation.

These reactions will cause a structural change in the physical and optical properties of the polymer. Any change in the polymer properties relative to the initial, desirable properties is called degradation. In this sense, "degradation" is a generic term for any number of reactions, that are possible in a polymer. A polymer can suffer from mechanical degradation when it is exposed to different kind of external forces, leading to fatigue and rupture. When it is exposed to the action of different solvents or hydrolysis, the polymer will be exposed to chemical degradation. Biodegradation refers to the exposure to microorganisms that decompose the polymer and degrade it.

When a polymer is heated, thermal degradation occurs and chemical bonds start to break or disrupt, forming new and different molecules. Thermal degradation always occurs when transforming a polymer because the polymer is exposed to heat. Polypropylene is normally processed at a range of temperatures between 220 and 280° Celsius and needs a stabilizer to prevent degradation.

The polypropylene twine used in this study is subject to some mechanical forces that keep the twine in place under the plants' weight, a maximum of 15 pounds per twine. Heat would not be a concern since this twine is used in the highlands where the temperatures never exceed 23° to 25° C (INSIVUMEH 2003).

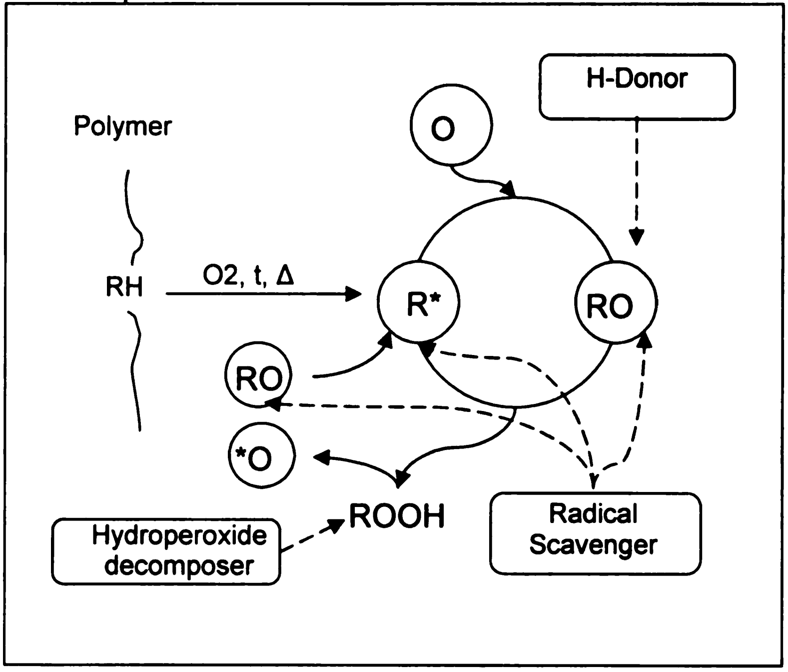
- Photoxidation degradation

Exposing polymers to sunlight and some artificial lights that generate UV radiation can have destructive effects on plastic products. UV radiation can break down the chemical bonds in a polymer. Photodegradation occurs when the polymer have been exposed to UV light. In the air there is oxygen present and simultaneously to Photodegradation, oxidation can occur. This phenomenon will be called photoxidation. The UV light emitted by the sun is absorbed by the polymer molecules, creating free radicals that decompose the polymer. Polypropylene has C-C bonds and C-H bonds that both can be dissociated by UV light energy (300 to 400 nm). (Selke 2003).

Titanium Dioxide is one of the most important white pigments for polymers. Its most important characteristic is the ability to promote in presence of UV light a oxidation process. The surface will pulverize and will exhibits a phenomenon call chalking (Gätcher and Müller, 1983).

Photodegradation causes cracking, chalking, color changes and the loss of physical properties observed in the samples from Guatemala. The black polypropylene twine is no longer black but tends to have a grayish color, and small filaments breaking and fall off the original net structure of the twine. Figure 14 shows how free radicals are formed in a polymer that is exposed to UV light as a consequence

Figure 14. Mechanism of antioxidant action
Source: Special Chem 2004



Photodegradation in the polyolefin family is generally due to the presence of catalyst residues, hydroperoxide groups, carbonyl groups and insaturation of the bonds introduced during the processing of the polymer. In polypropylene, isolated hydroperoxides can be formed, and then they start grouping in different way. Then oxidation occurs and may end in a chain scission. The B-scission reaction has been considered mainly responsible for polypropylene degradation. It is sometimes difficult to separate photodegradation from oxidation.

The aliphatic polyamides are polymers that only absorb a small amount in the short wavelength region of the sun's light spectrum. The absorption is due to the impurities present in the polymer. Direct chain scission will occur and photoxidation will occur in the outside layer of the polymer. Nylon monofilament is made from an aliphatic polyamide, and was chosen as a possible solution because it theoretically will behave differently than polypropylene, it can be found in the Guatemalan market, and it is available at a reasonable price.

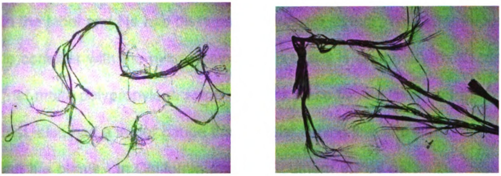
Black polypropylene twine has carbon black as an additive and a pigment the degradation will be different than for white polypropylene that has titanium dioxide as a pigment but does not have any UV light absorber (Stepek and Doust 1983).

Chapter 3
Methodology.

Materials

Growers in Guatemala provided samples of used and degraded twine. Figure 15 (A) shows the material as it appears after having been exposed to two years in the fields.

Figure 15. Samples exposed for two years provided by the growers in Guatemala (A) and sample exposed after 1152 hours in the QUV machine (B).



(A) (B)

For this series of experiments the black polypropylene twine was purchased in Guatemala City following the brand and the specifications of the growers. To demonstrate hypothesis number two, that black polypropylene twine absorbs light differently than white polypropylene, white polypropylene was also purchased.

Black polypropylene had carbon black as additive to prevent photodegradation, white polypropylene had white titanium dioxide as a pigment and did not have any UV stabilizer (Salguero 2003). The quantity of each additive could not be determined due to proprietary formulating.

Nylon was purchased in the United States from a local retailer. It was sold as fishing line and comes in rolls of 20 yards. Knowing the weight that will be exerted on the twine is equivalent to 15 pounds, line rated for 30 pounds resistance was chosen, with the expectation that when it was degraded by half, the plants would still be able to be supported by the nylon twine. N1 and N2 were fishing lines were labeled extra strength and with a greenish tint. N3 and N4 were normal transparent fishing line, the same brand, and 75% less expensive than the first two samples. N3 had twenty-five pound strength stated in the label and N4 had thirty-pound strength stated. The other important aspect to consider with the nylon fishing line is that it is a monofilament, contrary to the "net-multi- polypropylene twine". Since these fishing lines had the higher pound test, also had a larger gauge than regular fishing line and would not be sharp and cut the plants. In California and the Southern states galvanized iron is used for this purpose, and the idea was to simulate the same gauge of the iron with the fishing line. Previous experiments in Guatemala using very fine fishing line produced good results for degradation, but cut the plants (Santizo 2003).

Weathering tests are very useful in packaging because some packages will be exposed for certain amounts of time to different weather conditions, and it is necessary to observe how they will behave under these different conditions. For example, in the School of Packaging, polypropylene woven bags for food aid have been analyzed for the USDA, to see the expected behavior in case they will have to be stored outdoors. Other examples are plastic films and fabric used in agriculture and sand bags and how they behave outdoors. These concerns focus on how much time they can be in the fields, how they will degrade and what kind of residues they will leave behind (SpecialChem 2003). For packages, ultraviolet test devices made by Q-Panel Co. and Atlas Electric Devices Co have been used. (ASTM D4329)

A QUV/SE Accelerated Weathering Tester, manufactured by Q-Panel Company, Cleveland, Ohio, was used for this series of experiments. This apparatus complies with G53 (ANSI 1992) and with ASTM D4329.

The QUV machine has 24 positions available for testing and has to be full in order to operate. The samples were mounted on aluminum plates, tied in the back into a knot and pressed into the holders by snap rings. Figure 16 shows the different parts of the fixtures, and Figure 17 shows a view of the QUV apparatus.

Figure 16. QUV machine mounting fixtures.

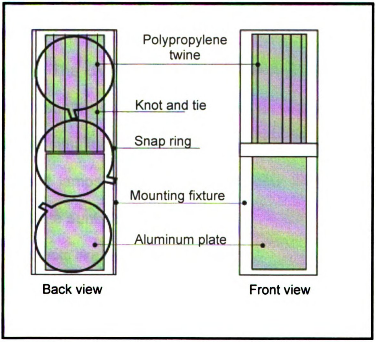
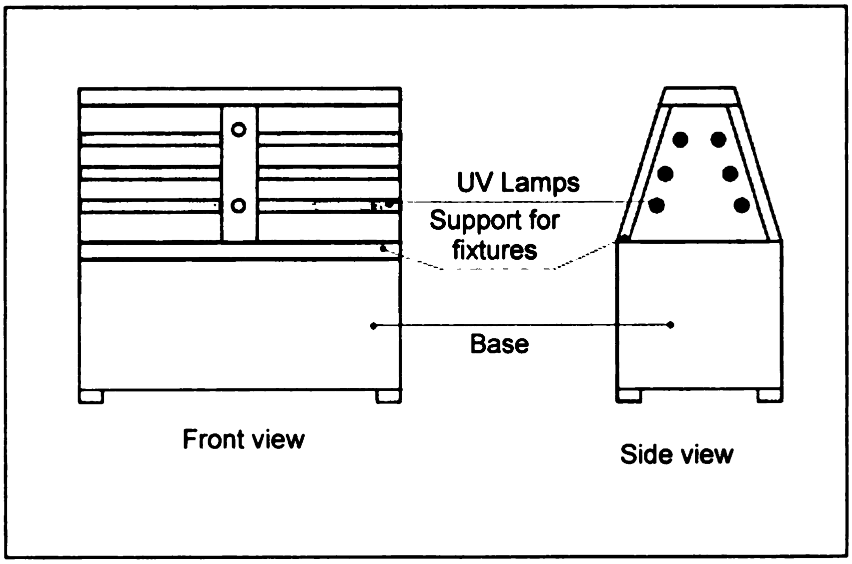


Figure 17. View of the QUV Machine



There are four kinds of fluorescent lamps in a QU-V machine: two types of UV-A lamps with the higher wavelength and two types UV-B lamps that produce the UV-B wavelengths. They look like ordinary fluorescent lamps but produce mainly UV light.

The UV-A lamps are recommended for tests comparing generic plastics, and usually do not degrade materials as fast as UV-B lamps. UV-A 340 lamps better simulates sunlight in the range between 365 nm and 295 nm and are the default lamps proposed by the ASTM D4329. UV-A 351 lamps are used to simulate sunlight filtered by a window and is generally used to test the behavior of objects like automotive interiors.

The UV-B lamps reproduce the wavelengths that degrade polymers and cause damage outdoors and this is why they are usually used for simulating outdoor degradation. These lamps have demonstrated a good and accurate correlation to outdoor exposures for evaluating material integrity of polymers. These lamps provide the fastest and most cost efficient exposure. Two different types of UV-B lamps are available; they produce the same UV wavelengths but different amounts of energy. Both of them emit 313 nm of UV-B light spectrum, UV-A light and some visible light. QSF-40, also known as FS-40 or F40UVB is generally used to test automotive interiors and coatings.

UV-B 313 was designed for QUV testing: it produces higher UV output and faster results than QFS-40. For this experiment, UV-B 313 lamps were selected because they produce the UV-B wavelength and will produce faster and more cost effective tests.

The main difference between weathering testers and outdoor exposure is the reproducibility of the results. Light, temperature and moisture are controlled by the QUV machine. For this experiment the condensation period was omitted in favor of having UV light exposure. The reason for this decision was that polypropylene was not expected to be degrading because of moisture. Nylons can be susceptible to water, but since the samples were fishing lines, and to replicate the experiments, the same considerations were taken for the nylon testing.

The QU-V apparatus can recreate outdoor exposure, but it is necessary to remember that other elements as geographic position and topography can affect the results (ASTM D 4329 1992). The areas where these crops are planted have a range of temperature of 15 to 25° Celsius. The QU-V apparatus was set to a temperature of 60° Celsius, with a irradiance level of 1.20 ± .05 W/m2/nm @ 313 nm, the highest irradiance possible. These parameters were selected to cause a faster rate of degradation, and to be able, in a short time, to correlate to the two year degraded samples provided by the growers.

Control of iridescence, the rate at which light energy falls on a unit area of surface, is extremely relevant because the smallest discrepancy will affect the results (Q-Panel 2003). The QU-V machines are equipped with an automatic irradiance control that uses a "solar eye" that allows the control of the irradiance continuously and is maintained automatically. Four sensors placed in the sample planes control and compensate for lamp aging and any other variability by adjusting the power to the lamps. Rotating and replacing the two oldest lamps every 400 hours also helps to compensate. Each lamp has a life of 1600 hours, and replacement only takes five minutes.

Lamps were rotated during the different experiments every 400 hours and then the solar eye was also recalibrated. Figure 18 shows the rotation of the lamps and in Figure 19 a sample of the "solar eye" panel is displayed.

Figure 18. Lamp Rotation
Source: Q-Panel Technical Bulletin LU-8160. *A choice of lamps.*

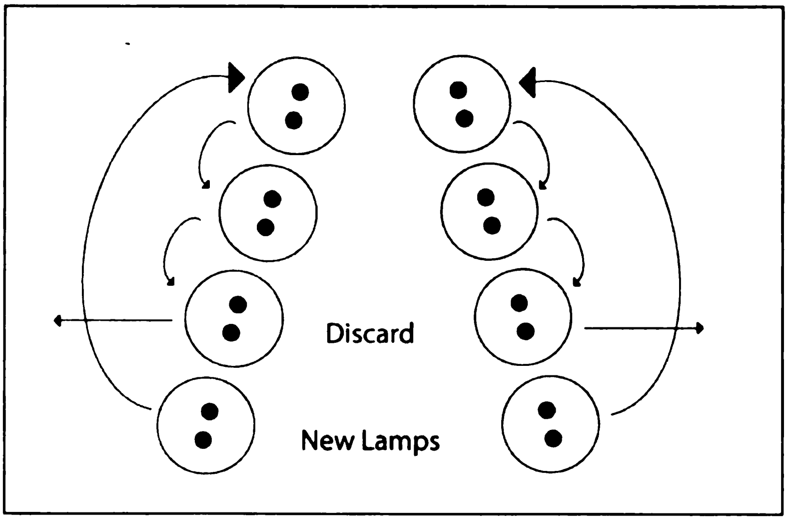
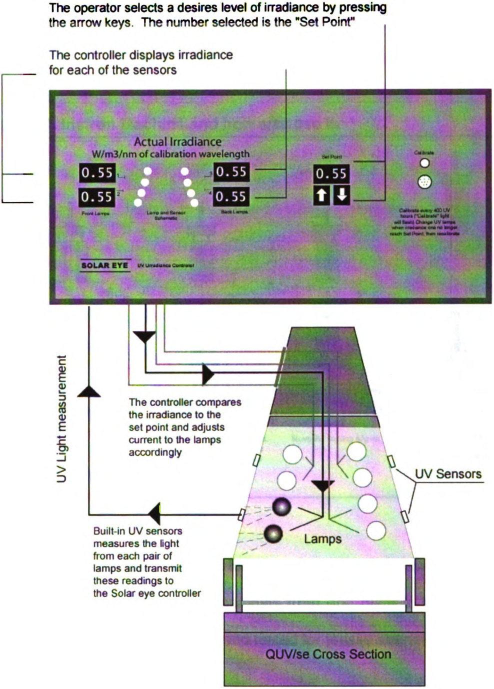


Figure 19. Solar Eye Panel
Source: QU-V Bulletin Lu-8160 1994



The operator selects a desires level of irradiance by pressing the arrow keys. The number selected is the "Set Point"

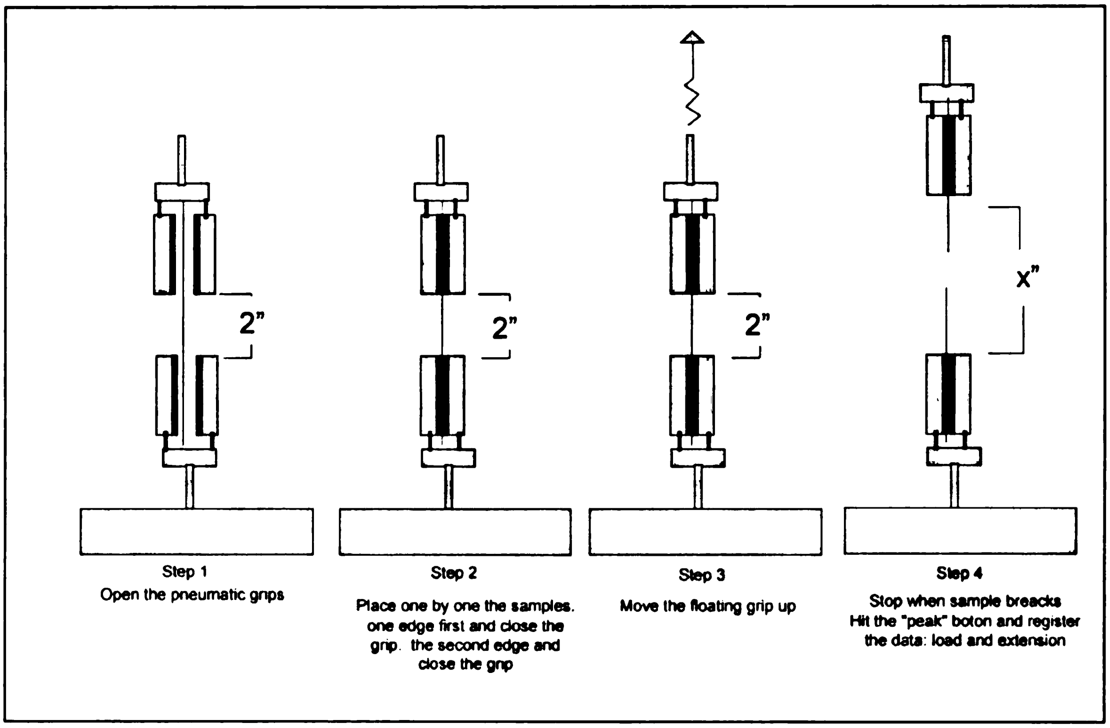
The controller displays irradiance for each of the sensors

The controller compares the irradiance to the set point and adjusts current to the lamps accordingly

Built-in UV sensors measures the light from each pair of lamps and transmit these readings to the Solar eye controller

ASTM D 638-99 Standard Test Method for Tensile Properties of Plastics procedure was followed for tensile testing. First 10 non-exposed samples were tested on an Instron machine model 4201, which has a constant-rate-of-crosshead-movement mechanism and grips that hold the specimens. The grips were separated by two inches, as shown in Figure 20. This machine is in compliance with the requirements of ASTM D 638-99.

Figure 20. Instron Machine and how was use it.



For each sample, the peak load and the extension were registered by the machine. Every 144, hours 10 samples from one plate in the QU-V machine were cooled to room temperature and tested for tensile strength in the Instron.

Sample preparation

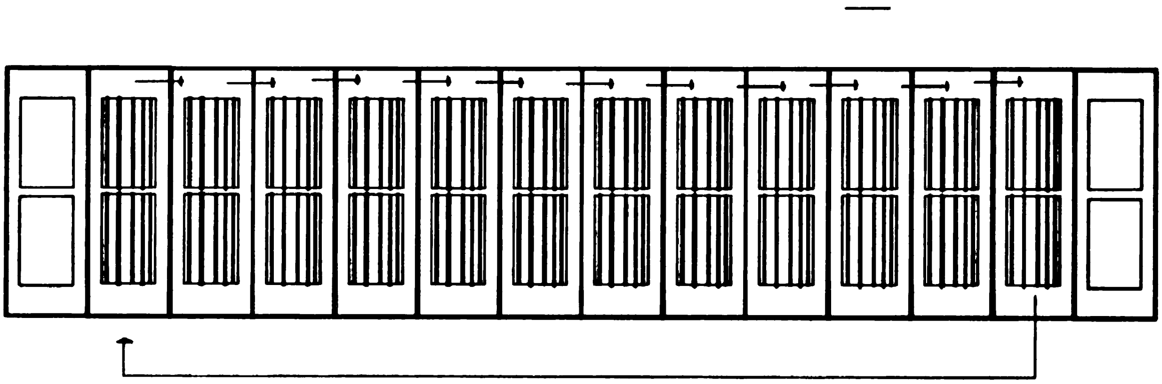
First the outside layer of the roll was discarded and the samples were cut from an inside layer of the roll. Each sample measured 15 inches (38.1 cm). It was wrapped around the aluminum plate of 0.635mm thickness as required by ASTM 4329-92, and to tied to a nut. Then the samples were trimmed to 3 inches after the nut and tie. The plates were mounted on the fixture and tightened with the snap rings. On each plate five samples were mounted, since ASTM 4329-92 requires at least 3 replications of the samples. Then they were placed in the QUV machine for running the experiments. The QUV machine is located in a laboratory at Michigan State University at the School of Packaging with controlled conditions between 18° and 27° degrees Celsius and is in compliance with the same standard test procedures. Four different tests were run as described below.

Experiments Performed

For this experiment a total of four experiments were done: a pilot test, black polypropylene twine, one using black and white polypropylene twine and a last one with four different nylon fishing lines. In all the tests the parameters and procedures were the same. Every plate had 5 samples tied in the back and fixed to the fixture by the snap rings. Every 144, hours fixtures were rotated as suggested by ASTM D 4329 and as shown in Figure 21.

Figure 21 Side-to-Side Rotation

Source: ASTM 4329-92



During the course of the four experiments, temperature was constant at 60° C with a setting point of 110 on an irradiance level of 1.20 ± .05 W/m2/nm @ 313 nm. During the total test time, the QUV apparatus was in exposure mode only, and used UV-B 313 lamps.

Except for the black and white polypropylene experiment that was run for only 144 hours, the experiments were run for 1152 hours. Every 144, hours a fixture was removed from the machine and the samples were tested for tensile strength.

- Pilot experiment

For the pilot experiment all of the 48-aluminum plates were filled with the black polypropylene twine, making a total of 240 samples, and mounted in the QUV apparatus.

After 1152 hours of continuous exposure the samples began to look like the samples brought from the fields and were already disintegrating in a hair-like shape. Once the baseline exposure time was determined (1152 hours), a second experiment was run.

- Black twine experiment

This experiment was a replication of the pilot test and was to correlate the results after the different periods of time. The 48 aluminum plates were filled with the black polypropylene twine, making a total of 240 samples, and mounted in the QUV Machine.

Every 144 hours a sample was removed from the machine and tensile tested. The experiment continued up to 1152 hours, time indicated by the experiment.

- Black and white twines experiment

For this experiment, the QU-V Machine was loaded with half of the mounting fixtures (12), 24 plates with black polypropylene twine and the other half with white polypropylene twine, giving a total of 120 samples per twine.

After144 hours the experiment was terminated due to disintegration of the white twine

- Nylon experiment

After the results of the white polypropylene twine experiments, a solution still needed to be found and so an experiment was done with four (4) different nylon fishing line. The procedure was identical but this time 6 fixtures were loaded with 10 twines of each sample (N1, N2, N3 and N4)

Chapter 4
Results

Load (pounds) and extension (inches) as a function of time were the parameters for the study. Load refers to how many pounds are necessary to apply to the twine before rupture. Extension refers to the elongation of the twine before rupture. These two elements were tested every 144 hours on ten samples. The average of these ten results is reflected in the following figures.

In Figure 22, the results of the load in the pilot test and the confirmatory black twine test are compared, and in Figure 23 extension results are shown.

Figure 22. Average breaking load of black polypropylene twine during the pilot experiment and confirmatory black twine experiment.

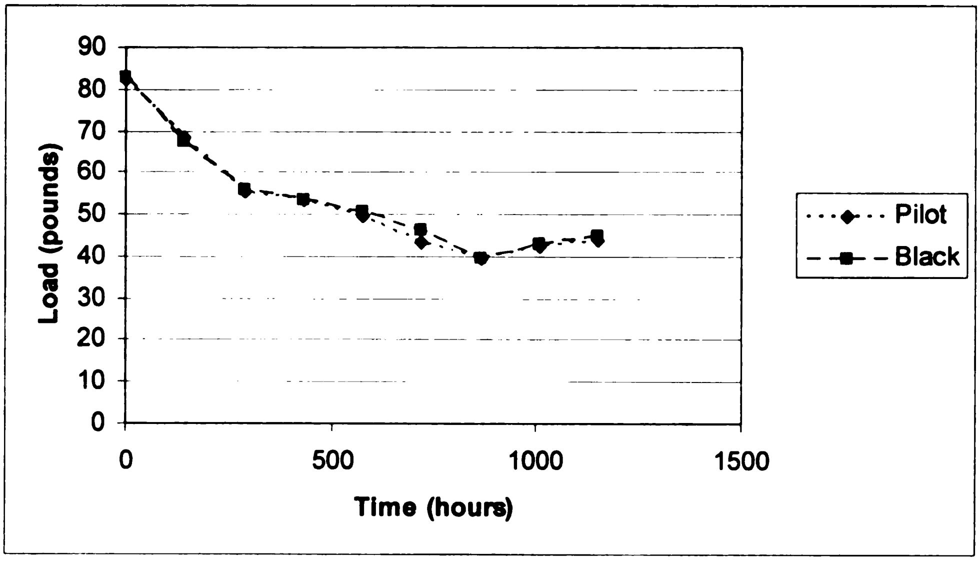
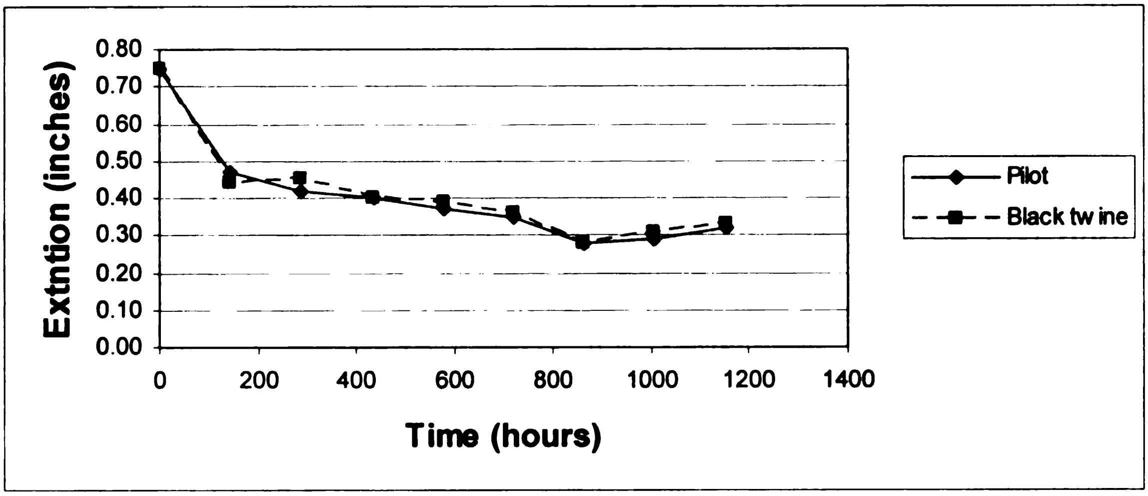


Figure 23. Average extension at break of black polypropylene twine during the pilot experiment and confirmatory black twine experiment.

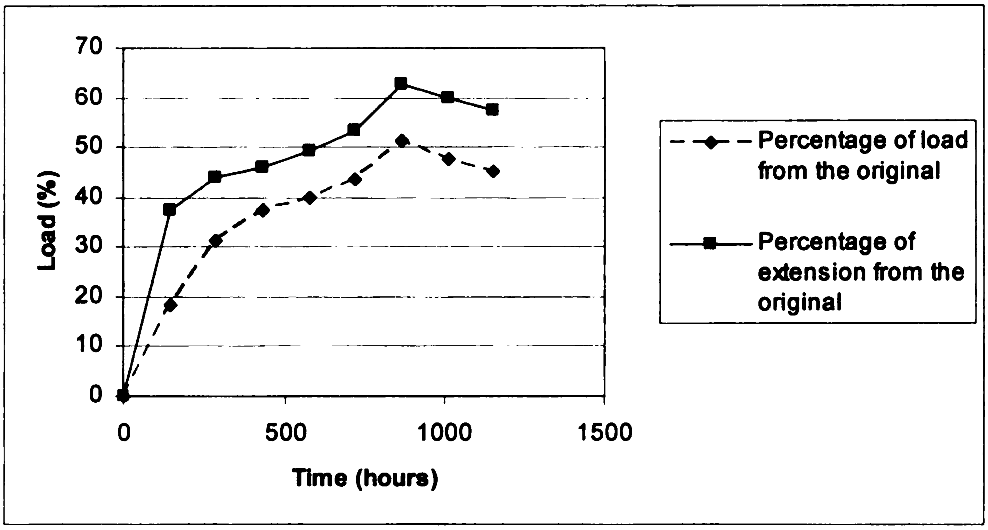


Clearly, during both tests the black polypropylene had the same behavior, for both load and extension.

The unexposed black twine has a tensile strength of 80 pounds. After 144 hours of exposure in the QUV apparatus, the black twine lost 12.5% of its original tensile strength. It was not until 864 hours that black twine lost 50% of its original tensile strength. After 1008 hours of exposure the black twine gained 3.75% from the last tensile test. After 1152 hours it gained 2.5% more tensile strength. This data is shown in Table 11 in Appendix 1.

The unexposed black twine has an extension at break of 0.75 inches. After the first 144 hours of exposure, the black twine had 37.33% less extension than the unexposed twine. Compared with the loss of tensile strength, the flexibility suffered more during this period of time. After 576, hours the black twine lost 50% of the original extension, 288 hours before the tensile strength reached that same 50% loss. After 864, hours the black twine had the lowest extension during the test with 62.66% loss. During the following 288 hours, the extension increased by 2.66% of the most recent value for each 144-hours period. These results are shown in Table 12 in Appendix 1, and a comparison between these extension percentages and load percentages are shown in Figure 24.

Figure 24. Comparison of load and extension percentages lost during exposure time.

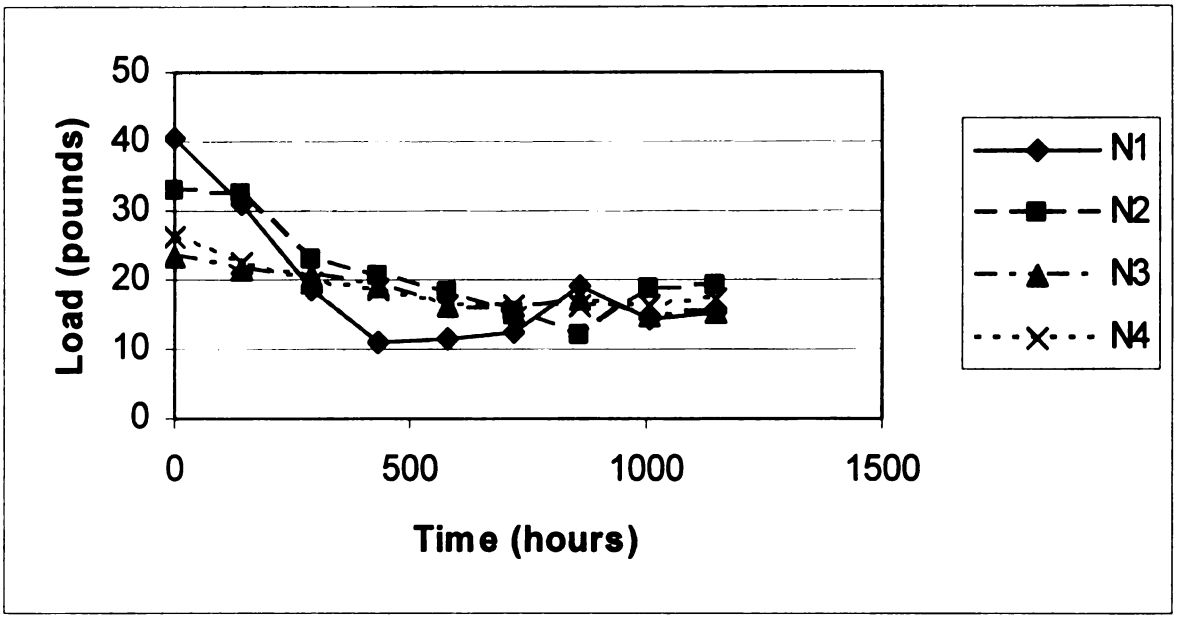


The percentage of load lost was higher than the loss in extension, but both followed a similar pattern.

The third test compared black polypropylene twine to white polypropylene twine. They were manufactured by the same company, and the difference between them is basically the additive and pigment they have. Black twine has carbon black as a pigment, which at the same time is a UV light stabilizer (Stepeck and Daoust, 1983). White twine has titanium dioxide as a pigment but it is not a UV stabilizer. Because white absorbs less light than black it was hypothesized that the UV light activity would not start oxidation in the white twine as quickly, therefore resulting in a different pattern of degradation. However, after the first 144 hours of exposure, the white twine was pulverized, and the test was discontinued.

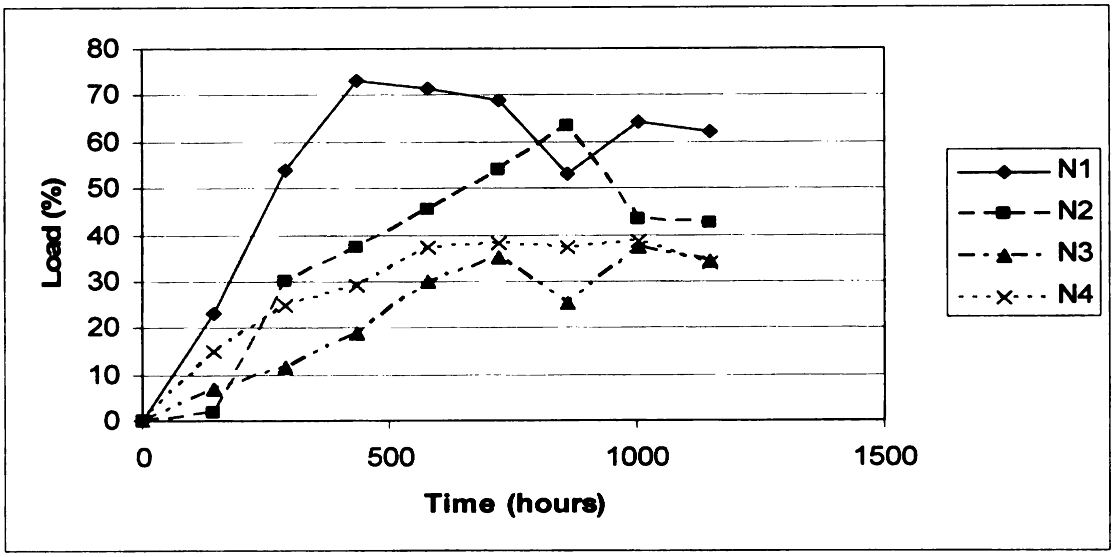
The fourth test was analyzing four different nylon twines. In Figure 25 the average load for each of the nylons is shown.

Figure 25. Average load of four nylon twines.



N1 and N2 were labeled "Extra Strength" and N3 and N4 were regular fishing lines. N1 had the highest initial tensile strength, 40 pounds, followed by N2 with 33 pounds, N4 with 26 pounds and N3 with 23 pounds. N1 and N2 had higher tensile strength through 144 hours of UV exposure; after 288 hours they had lost almost half of their tensile strength. In contrast, N3 and N4 had a more stable pattern of tensile strength. All four recovered some tensile strength after 720 hours of exposure. Because these are monofilaments, the outside layer of the twine got degraded and felt "sticky" to the touch. After this first layer was degraded, the inner layer was exposed and had similar properties to the original non-exposed twine but with a smaller gauge, requiring less loads to rupture. Figure 26 shows the percentages of tensile strength loss for the nylon samples.

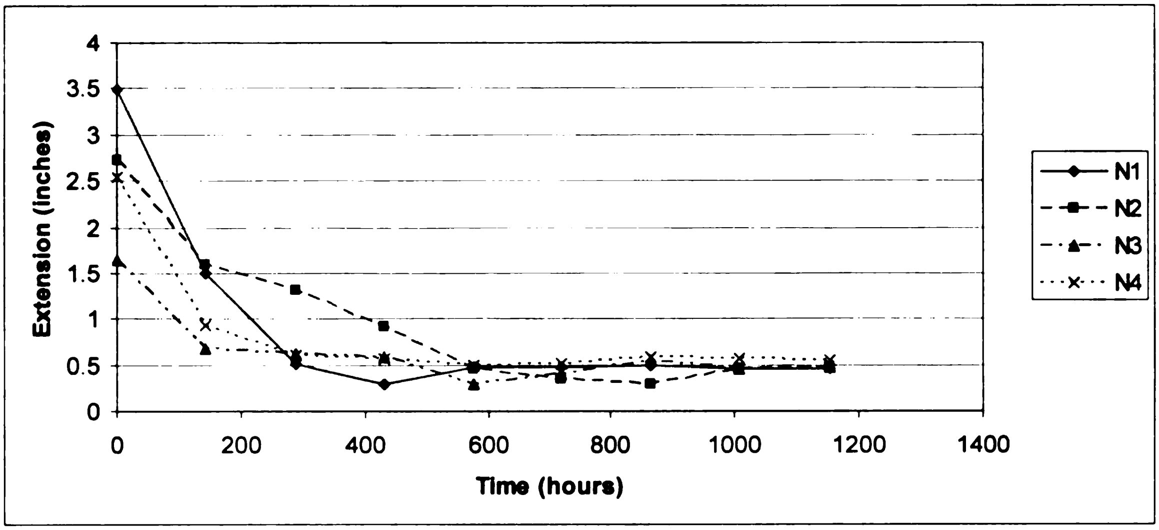
Figure 26. Nylon percentages of tensile strength loss



N4 will show the most stable pattern, compared to N1 and N2 that had a very disrupt pattern. N3 has also an increasing pattern with a slight decrease after 864 hours. After this decrease will increase and match N4 pattern.

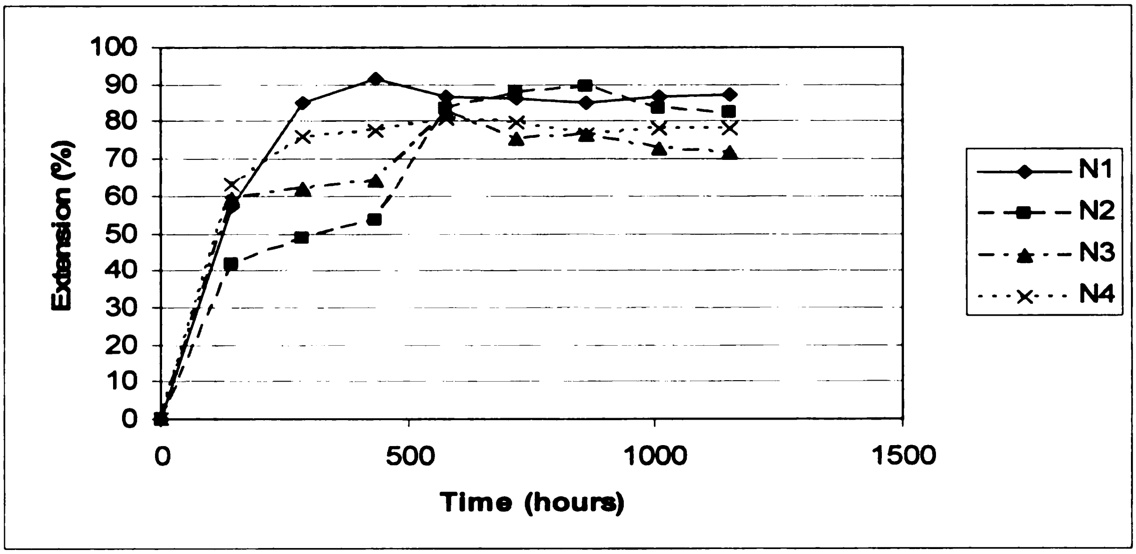
At zero hours, N1, N2, N3, and N4 had a long elongation before rupture, but after UV light exposure this elasticity decreased considerably, as shown in Figure 27.

Figure 27. Average extension of four nylon twines.



N1 had the highest initial extension of 3.5 inches. N2 and N4 were very close together with initial extensions of 2.72 and 2.53 inches, respectively. N3 had the lowest extension of the four samples with an initial extension of 1.65 inches. The four nylon samples had a significant drop in extension after the first 144 hours of exposure. After 576 hours, extension of the four samples was very similar, ranging from 0.7 inches to 0.5 inches. Figure 28 shows a comparison of the percentages of the extension lost over time for the four nylons.

Figure 28. Nylon percentages of extension loss



Again, N4 is the one that has a more stable behavior, but all four after 144 hours had lost at least 40% of their extension capacity. N2 has lost up to 60% after the first 144 hours, but after 576 hours it will gain 40% of the extension. All four after 576 hours will be close in their behavior ranging from 90 to 70% loss.

The total weight of the plants will not exceed fifteen pounds and there are 5 lines. Dividing the total weight by number of lines, the maximum force exerted per line is expected to be 3 pounds.

Stress is defined by the following formula:

Stress = Load (pounds) / Area (sq inches)

Stress = 3 /0.05

Stress for 3 pounds = 60 psi

As mentioned before, there is concern about the high elongation rate of the nylon, but looking at Figure 29 and Figure 30, it can be observed that the percentage of elongation will be less than 1% when the maximum expected weight is applied. This is true for N3 and N4 both after 0 hours of exposure and after 1152 hours of exposure.

Figure 29. N3 Stress-Strain curve

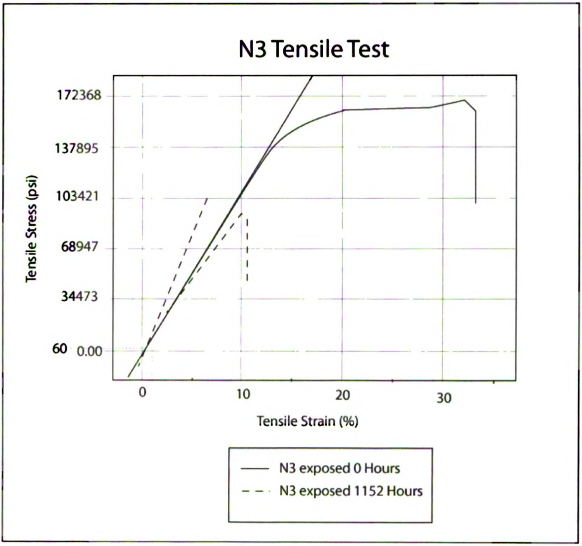
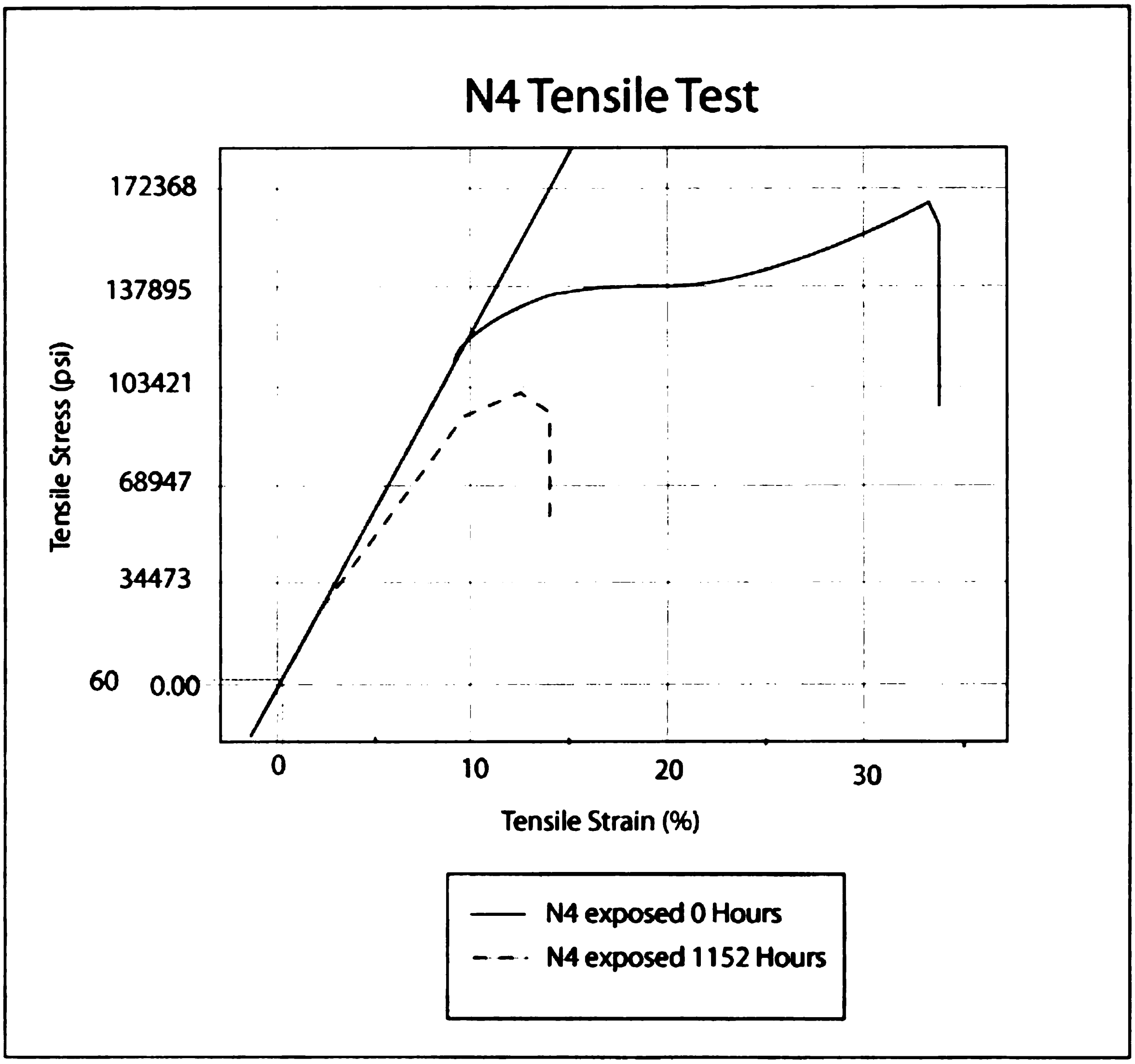
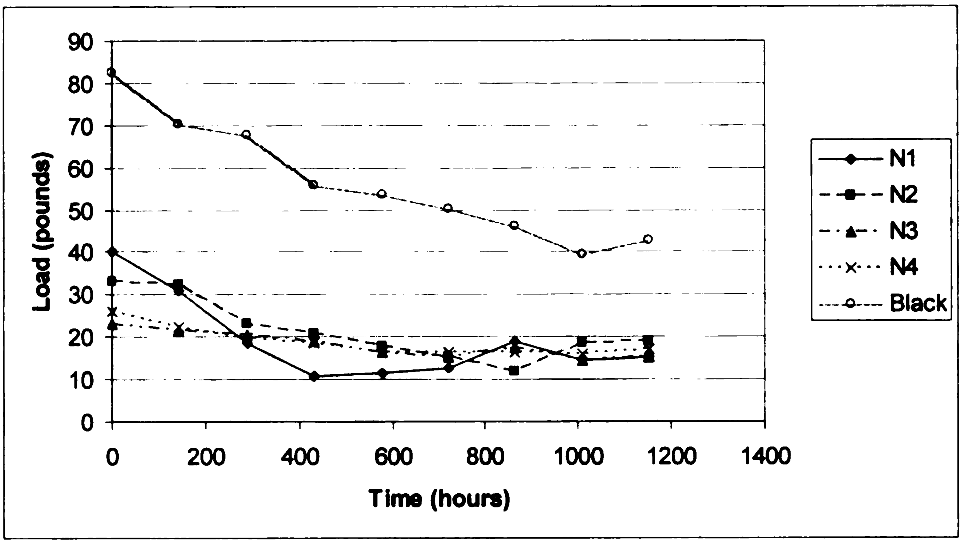


Figure 30. N4 Stress-Strain curve



Since white was rejected as a possibility the black twine and the four nylons were compared and analyzed. Figure 31 shows the behavior of these five different twines regarding the load and Figure 31 the extension in function of time.

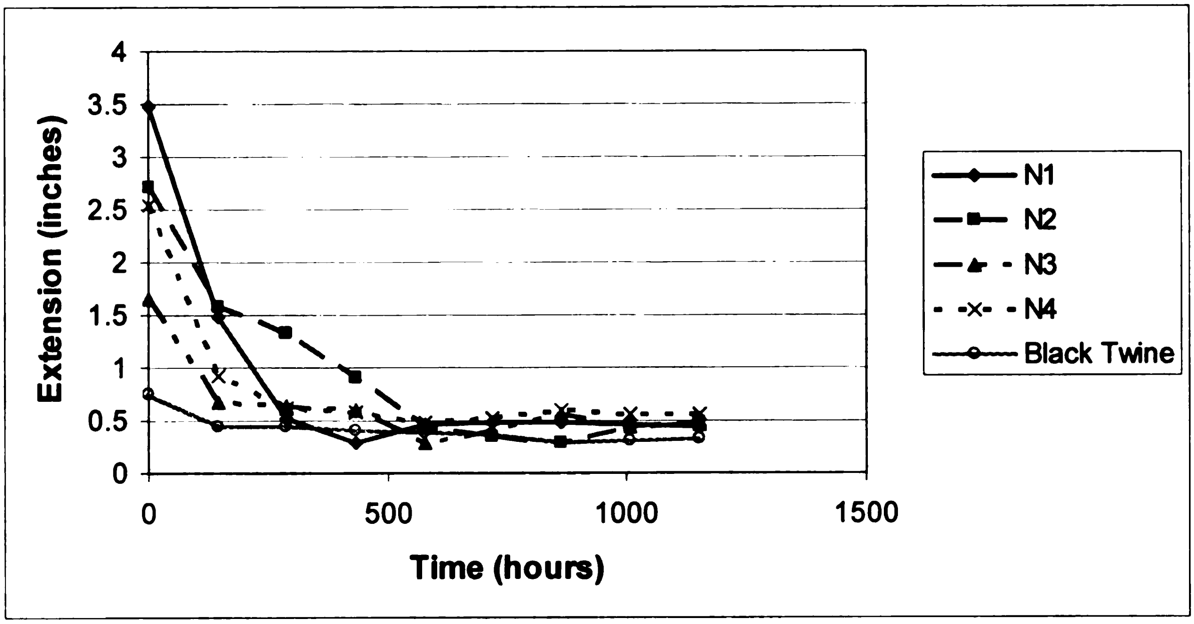
Figure 31. Average load of four nylon twines and black twine.



Black twine supports a higher load than nylon. But, black twine has a larger gauge than nylon. Black twine has almost doubled of the tensile strength the nylon, but also has 3 times the gauge. It is important to notice that the five materials have a similar behavior when exposed to UV light. They decrease considerably their tensile strength at the beginning and they later recuperate part of what was lost. The main difference with this material will be that the black twine is a multifilament and the filaments are thin enough to rupture after the first hours of exposure, and the nylons are a monofilament and it will take longer for degradation to reach the inner layers.

After, UV light exposition the twine extension has a different behavior. Figure 32 shows the average extension of nylon and black twine.

Figure 32. Average extension of nylon and black twine



At the beginning, black twine has a lower capacity of extension, only 0.75 inches compared to nylons that range from 1.5 to 3.5 inches when before to UV light exposition. But after 576 hours of exposure, all five samples have on average 0.5 inches of extension. Thus, UV light not only affects the tensile strength properties but also the elasticity properties. This is explained by the fact that polypropylene is more brittle than nylon, and nylon is more flexible at lower temperatures (Rodriguez 1996). The other explanation is that black twine is a multifilament with a net structure, as some of the outside layer filaments start to degrade and break will have less tensile strength and less capacity of elongation.

Compared to the black twine, nylon, especially N3 and N4, is more stable on exposure to UV light.

Chapter 5
Conclusions and Recommendations.

After the experiments and analyzing the results, a solution to replace the polypropylene twine by 25-30 pound test nylon fishing line, was identified. This nylon monofilament should last more than 2 years in the fields, retaining more or less 50% of it initial strength. Since the total weight of the plant will never exceed 15 pounds, they should not break. In Table 3, an economic comparison between the nylon and the polypropylene twine is shown.

Table 3. Comparison of the costs of PP twine and nylon (1000 meters)

	Year 1	Year 2	Year 3	Removing filaments cost	Total
PP Twine	$ 7.50	$ 3.75	$7.50	Yes	$ 18.75 + extra packing costs
Nylon	$ 2.00	0	0	No	$. 2.00

If a monofilament did break, the farmers would have to replace the damaged section with a newer one. This will lead to an operational and administrative need to inspect and replace the line, when necessary. This activity could be done during the regular inspections for pests and diseases, during the harvest time or during the planting season of both crops: snow peas and broccoli. It will be recommended that every time a worker is out in the fields he carries with him a roll of the nylon monofilament for replacing lines as needed. After 2 years of exposure, it is recommended to replace all the lines to avoid collapsing plants and return to lines with full strength.

It is necessary to conduct field research to correlate these results with natural exposure to UV light and other possible concerns. For this purpose, it is recommended that the twine in one plot of a snow pea field be replaced by N3 and another with N4. Since the only correlation between the natural exposure and the QU-V machine is that probably 1152 hours correlates to about two years, the field should have to be monitored every week. Every week, observations should be written in a notebook, especially when the black twine begins to break. The time when this is happening can be clearly established, providing correlation to the QUV machine.

For further studies it will be interesting to conduct an experiment with polypropylene twine with different quantities of carbon black to see the differences in degradation correlated to the different percentages of carbon black present in the twine. If the results are positive, this could lead the polymer industry in the region to find markets, even if the price is higher.

Due to economic and time constraints, it was not possible to evaluate performance in the snow pea and broccoli plots, but the laboratory results obtained represents a guide to more research in the fields. Finally, for further laboratory research, it is recommended to try a polypropylene monofilament and compare the results with the nylon monofilament.

Appendix 1

Results from tests (tables)

Table 4. Load (in pounds) of black polypropylene twine as function of time during pilot experiment.

Pilot Project								
Sample	0 Hours	144 Hours	288 Hours	432 Hours	576 Hours	720 Hours	864 Hours	1152 hours
1	82.15	65.25	60.25	46.89	48.67	36.99	40.37	38.99
2	72.5	63.03	54.3	47.55	40.11	38.57	35.67	34.76
3	77.34	62.04	58.99	58.99	52.43	48.56	39.99	35.66
4	85.06	66.01	54.03	59.87	52.46	43.76	46.84	50.87
5	82	75.76	56.98	55.76	50.01	42.56	40.14	40.23
6	83.9	70.35	51.99	48.56	49.99	40.18	39.23	45.78
7	85.77	67.15	55.54	52.47	50.65	43.45	45.66	34.42
8	86.89	73.99	44.98	59.78	52.65	50.11	42.79	43.76
9	79.47	67.43	49.89	51.23	50.65	48.37	33.65	48.9
10	86.78	72.89	64.57	54.87	48.99	39.99	32.45	49.3
Average	**82.19**	**68.39**	**55.15**	**53.60**	**49.66**	**43.25**	**39.68**	**42.27**
DVST	4.62	4.68	5.54	5.02	3.64	4.51	4.74	6.31

Table 5. Load (in pounds) of black polypropylene twine as function of time during black twine experiment.

Black PP Twine								
Sample	0 Hours	144 Hours	288 Hours	432 Hours	576 Hours	720 Hours	864 Hours	1152 hours
1	83.14	64.75	60.51	47.68	50.68	37.85	44.67	40.54
2	71.7	62.76	53.21	48.05	38.58	52.94	30.6	35.49
3	77.26	61.1	59.46	58.68	51.25	51.06	40.27	55.03
4	87.01	65.29	54.17	62.47	48.91	41.82	43.11	43.01
5	83.49	72.59	55.41	53.1	54.66	42.09	35.01	42.85
6	82.6	69.91	51.11	46.55	51.11	43.27	38.66	42.71
7	85.66	66.42	56.38	53.72	55.73	47.13	41.23	34.42
8	89.77	74.01	48.16	56.27	55.73	53.69	42.9	45.1
9	81.34	66.2	55.35	54.52	44.99	51.76	39.25	45.15
10	84.19	73.07	62.68	55.01	51.81	38.07	37.23	43.49
Average	**82.62**	**67.61**	**55.64**	**53.61**	**50.35**	**45.97**	**39.29**	**42.78**
DVST	5.09	4.52	4.39	5.06	5.26	6.12	4.21	5.67

Table 6. Initial strength of black and white twine (144 hours)

Sample	White Twine	Black Twine
1	82.34	83.14
2	80.09	71.7
3	72.34	77.26
4	73.46	87.01
5	76.89	83.49
6	78.48	82.6
7	80.01	85.66
8	85.33	89.77
9	70.45	81.34
10	75.69	84.19
Average	**77.51**	**82.62**
DVST	4.65	5.09

Table 7. Elongation of black and white twine (144 hours)

Samples	Black Twine	White Twine
1	0.555	0.465
2	0.497	0.567
3	0.985	0.774
4	0.717	0.776
5	0.991	0.998
6	0.901	0.756
7	0.868	0.769
8	0.761	0.865
9	0.591	0.645
10	0.598	0.678
Average	0.75	0.73
STD	0.18	0.15
%	100	100

Table 8. Load (in pounds) in relation to time for N1

N1	0 Hours	144 Hours	288 Hours	432 Hours	576 Hours	720 Hours	864 Hours	1152 hours
1	42.3	17.81	35.67	9.981	11.46	12.25	18.9	13.61
2	41.21	33.44	29.85	8.284	10.89	11.002	18.78	14.14
3	42.28	31.48	17.211	10.65	11.85	12.5	20.51	15
4	39.49		14.24	14.2	21.03	15.3	16.78	14.23
5	43.87	33.9	30.56	8.757	6.776	10.85	21.7	12.71
6	39.44	32.78	7.25	8.44	24.03	16.85	20.36	14.54
7	36.64	30.2	17.84	11.11	7.29	10.54	18.58	14.88
8	36.4	31.57	15.72	12.56	7.52	11.36	17.36	14.96
9	42.47	35.73	8.961	9.879	6.389	10.25	20.67	14.09
10	38.93	31.78	8.601	14.59	6.448	15.28	15.219	15.63
Average	40.30	30.96	18.59	10.84	11.36	12.61	18.88	14.37
DVST	2.54	5.19	10.06	2.27	6.28	2.34	2.00	0.82
%	100	76.81	46.12	26.89	28.18	31.28	46.84	35.67

Table 9. Load (in pounds) in relation to time for N2.

N2	0 Hours	144 Hours	288 Hours	432 Hours	576 Hours	720 Hours	864 Hours	1152 hours
1	33.89	34.11	23.33	18.94	16.71	15.98	15.43	19.64
2	29.41	30.35	26.61	18.12	20.89	18.15	10.83	18.84
3	31.14	28.22	25.62	18.67	14.14	12.13	7.329	20.35
4	35.64	32.99	22.07	22.88	17.72	15.89	11.13	19.7
5	34.94	31.36	25.68	22.21	19.18	16.25	10.1	16.07
6	32.23	33.72	20.76	16.65	22.95	12.88	17.28	17.16
7	35.66	34.59	23.1	24.15	23.6	14.89	10.13	21.05
8	32.28	32.82	24.01	24.92	17.13	15.78	11.11	17.96
9	32.32	40.8	18.01	23.36	11.58	14.25	12.59	19.48
10	31.86	24.23	21.7	16.74	16.36	15.45	14.31	16.58
Average	32.94	32.32	23.09	20.66	18.03	15.17	12.02	18.68
DVST	2.05	4.35	2.60	3.16	3.76	1.73	2.93	1.67
%	100.00	98.14	70.11	62.75	54.74	46.05	36.50	56.73

Table 10. Load (in pounds) in relation to time for N3.

N3	0 Hours	144 Hours	288 Hours	432 Hours	576 Hours	720 Hours	864 Hours	1152 hours
1	22.84	20.94	19.6	18.56	13.19	14.25	16.33	14.31
2	23.16	21.18	19.44	18.46	15.44	16.89	18.8	14.27
3	25.05	21.09	19.97	18.83	11.7	13.85	14.94	15.32
4	23.71	21.74	18.54	18.69	18.45	16.58	18.91	14.82
5	24.07	21.13	20.14	19.65	17.65	14.22	15.73	12.11
6	22.93	21.78	19.68	19.53	18.2	16.44	16.82	15.72
7	22.31	20.77	20.93	18.63	18.71	15.77	18.2	14.96
8	22.99	23.14	22.7	18.06	17.15	14.23	18.53	14.46
9	22.74	22.59	20.06	19.24	16.85	15.97	17.84	14.45
10	21.94		23.15	18.53	14.82	12.58	17.52	14.95
Average	23.17	21.60	20.42	18.82	16.22	15.08	17.36	14.54
DVST	0.90	0.81	1.45	0.50	2.37	1.44	1.36	0.97
%	100	93.16	88.12	81.2	69.97	65.06	74.92	62.72

Table 11. Load (in pounds) in relation to time for N4.

N4	0 Hours	144 Hours	288 Hours	432 Hours	576 Hours	720 Hours	864 Hours	1152 hours
1	27.22	21.93	21.27	16.61	16.31	16.25	15.65	15.44
2	19.37	21.44	18.02	18.03	16.05	17.01	13.47	16.11
3	22.85	22.08	18.01	15.51	17.19	15.89	16.67	17.13
4	27.74	23.17	20.82	17.2	15.74	15.23	16.9	16.52
5	24.16	22.86	21.08	19.26	17.36	14.75	17.21	16.44
6	29.05	24.18	18.79	18.42	15.3	15.54	16.79	15.82
7	24.98	21.58	18.58	19.73	17.66	16.85	16.9	16.82
8	27.79	23.11	21.13	20.66	15.75	17.05	17.07	16.18
9	28.28	21.32	16.69	21.24	16.21	16.32	17.08	15.55
10	29.54	20.27	21.26	18.1	16.48	16.98	16.41	14.67
Average	26.10	22.19	19.57	18.48	16.41	16.19	16.42	16.07
DVST	3.21	1.14	1.72	1.79	0.77	0.82	1.13	0.72
%	100	96.08	74.96	70.79	62.85	62.02	62.89	61.56

Table 12. Percentage load loss of black twine

	Percentage of load loss from the original	Difference in % between the previous period of time
0	100	0
144	87.5	12.5
288	31.25	18.75
432	37.5	1.2
576	40	2.5
720	43.75	3.75
864	51.25	8
1008	47.5	3.75
1152	45	2.5

Table 13. Percentage extension loss of black twine

	Percentage of extension loss from the original	Difference in % between the previous period of time
0	100	0
144	37.33	62.67
288	44	6.67
432	46	2.66
576	49.33	3.3
720	53.33	4
864	62.66	9.33
1008	60	2.66
1152	57.33	2.66

Table 14. Percentage load loss of nylons

	N1	N2	N3	N4
0	100	100	100	100
144	23.17	1.88	6.77	14.98
288	53.87	29.9	11.73	25.01
432	73.1	37.23	18.77	29.18
576	71.31	45.26	29.99	37.12
720	68.7	53.94	34.91	37.96
864	53.15	63.5	25.07	37.08
1008	64.34	43.29	37.24	38.42
1152	62.13	42.28	34.18	33.79

Table 15. Percentage Extension loss of nylons

	N1	N2	N3	N4
0	100	100	100	100
144	57.18	41.91	59.39	63.24
288	85.05	48.52	61.81	75.88
432	91.66	33.45	64.24	77.47
576	86.49	83.45	82.42	80.63
720	86.2	87.5	75.15	79.44
864	85.06	89.33	66.66	76.67
1008	86.78	83.45	72.72	77.86
1152	87.06	82.35	71.51	78.26

Table 16. Elongation in inches of black twine during pilot experiment

Pilot test								
Samples	0	144	288	432	576	719	863	1007
1	0.459	0.555	0.555	0.478	0.398	0.302	0.233	0.35
2	0.556	0.465	0.401	0.459	0.356	0.333	0.256	0.349
3	0.876	0.453	0.499	0.432	0.378	0.358	0.299	0.3
4	0.777	0.478	0.465	0.435	0.356	0.376	0.298	0.299
5	0.999	0.501	0.423	0.403	0.432	0.405	0.279	0.274
6	0.987	0.456	0.412	0.416	0.345	0.332	0.299	0.265
7	0.801	0.5	0.399	0.399	0.475	0.342	0.282	0.234
8	0.798	0.432	0.402	0.367	0.301	0.387	0.302	0.237
9	0.601	0.399	0.334	0.355	0.322	0.324	0.345	0.295
10	0.645	0.447	0.321	0.3	0.367	0.299	0.201	0.261
Average	0.75	0.47	0.42	0.40	0.37	0.35	0.28	0.29
STD	0.18	0.04	0.07	0.05	0.05	0.04	0.04	0.04

Table 17. Elongation in inches of black twine during confirmatory experiment.

Samples	0	144	288	432	576	719	863	1007
1	0.555	0.434	0.571	0.398	0.404	0.275	0.265	0.296
2	0.497	0.372	0.385	0.467	0.238	0.428	0.228	0.284
3	0.985	0.457	0.571	0.355	0.455	0.424	0.341	0.375
4	0.717	0.415	0.478	0.498	0.418	0.358	0.315	0.318
5	0.991	0.461	0.395	0.477	0.364	0.325	0.198	0.315
6	0.901	0.435	0.331	0.316	0.383	0.264	0.271	0.297
7	0.868	0.425	0.445	0.408	0.375	0.351	0.284	0.251
8	0.761	0.518	0.324	0.373	0.428	0.454	0.324	0.3
9	0.591	0.375	0.475	0.337	0.345	0.441	0.321	0.316
10	0.598	0.465	0.539	0.325	0.449	0.298	0.248	0.331
Average	0.75	0.44	0.45	0.40	0.39	0.36	0.28	0.31
STD	0.18	0.04	0.09	0.07	0.06	0.07	0.05	0.03

Table 18. Elongation in inches of N1.

Samples	0	144	288	432	576	719	863	1007
1	3.568	0.609	1.975	0.274	0.335	0.399	0.505	0.411
2	3.467	1.497	0.721	0.212	0.428	0.394	0.499	0.467
3	3.564	1.408	0.134	0.297	0.309	0.401	0.549	0.461
4	3.509	1.555	0.321	0.355	0.571	0.476	0.451	0.454
5	4.117	1.439	0.717	0.234	0.504	0.436	0.575	0.445
6	3.873	1.625	0.404	0.298	0.556	0.455	0.545	0.478
7	3.262	1.63	0.179	0.307	0.598	0.501	0.208	0.465
8	3.1	1.66	0.367	0.279	0.511	0.567	0.425	0.494
9	2.568	1.825	0.191	0.271	0.488	0.569	0.625	0.481
10	3.767	1.634	0.224	0.392	0.422	0.583	0.499	0.491
Average	3.48	1.49	0.52	0.29	0.47	0.48	0.49	0.46
STD	0.43	0.33	0.55	0.05	0.10	0.07	0.11	0.02

Table 19. Elongation in inches of N2.

Samples	0	144	288	432	576	719	863	1007
1	2.892	1.377	0.498	0.934	0.431	0.459	0.339	0.447
2	1.725	1.207	2.061	1.362	0.455	0.362	0.277	0.457
3	2.159	1.405	2.025	0.784	0.477	0.256	0.155	0.474
4	2.915	1.491	3.572	1.835	0.409	0.301	0.291	0.458
5	2.471	1.641	1.415	0.581	0.485	0.347	0.245	0.414
6	3.309	1.129	0.511	0.417	0.391	0.369	0.401	0.415
7	2.891	2.78	0.457	0.465	0.517	0.299	0.259	0.504
8	3.108	1.225	1.049	1.748	0.486	0.348	0.281	0.45
9	2.999	1.839	0.731	0.601	0.432	0.325	0.322	0.494
10	2.691	1.749	0.859	0.395	0.455	0.334	0.371	0.415
Average	2.72	1.58	1.32	0.91	0.45	0.34	0.29	0.45
STD	0.48	0.48	0.99	0.55	0.04	0.05	0.07	0.03

Table 20. Elongation in inches of N3.

Samples	0	144	288	432	576	719	863	1007
1	1.318	0.741	0.517	0.566	0.283	0.501	0.498	0.424
2	1.165	0.635	0.531	0.556	0.285	0.446	0.584	0.445
3	3.127	0.581	0.544	0.577	0.325	0.432	0.435	0.501
4	1.909	0.615	0.493	0.605	0.594	0.428	0.631	0.479
5	2.334	0.605	0.558	0.642	0.165	0.401	0.427	0.362
6	1.285	0.625	0.531	0.651	0.575	0.425	0.535	0.501
7	1.291	0.554	0.821	0.584	0.168	0.388	0.655	0.487
8	1.368	0.798	0.835	0.548	0.191	0.367	0.641	0.445
9	1.461	0.764	0.585	0.607	0.139	0.384	0.565	0.431
10	1.221	0.769	0.879	0.579	0.165	0.345	0.549	0.439
Average	1.65	0.67	0.63	0.59	0.29	0.41	0.55	0.45
STD	0.63	0.09	0.15	0.03	0.17	0.04	0.08	0.04

Table 21. Elongation in inches of N4.

Samples	0	144	288	432	576	719	863	1007
1	2.205	0.765	0.799	0.445	0.389	0.478	0.478	0.458
2	0.929	0.675	0.428	0.488	0.471	0.568	0.357	0.599
3	1.884	0.768	0.447	0.397	0.311	0.499	0.531	0.654
4	3.058	1.274	0.631	0.427	0.409	0.532	0.595	0.558
5	1.975	1.195	0.951	0.542	0.441	0.497	0.667	0.539
6	3.332	1.451	0.451	0.518	0.515	0.589	0.681	0.621
7	2.118	0.784	0.474	0.615	0.518	0.402	0.571	0.579
8	2.791	1.215	0.615	0.805	0.414	0.566	0.655	0.568
9	3.529	0.637	0.395	0.933	1.064	0.542	0.681	0.599
10	3.449	0.585	0.865	0.488	0.375	0.529	0.655	0.434
Average	2.53	0.93	0.61	0.57	0.49	0.52	0.59	0.56
STD	0.84	0.31	0.20	0.17	0.21	0.05	0.11	0.07

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