

**EFFECT OF RECYCLING ON MATERIAL PROPERTIES OF
POLYETHYLENE TEREPHTHALATE AT VARIOUS RECYCLING
RATIOS AND RECYCLING GENERATIONS**

By

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Abstract

Recycled plastics are considered low performance materials because their properties decrease with recycling. Resin manufacturers use rules of thumb to recommend recycled plastic usage, usually 25% or less by weight. These rules are very conservative, and are not based on sound experimentation.

The objective of this study was to begin to change current perception that recycled plastics are low-quality materials. For this purpose, the mechanical properties of a 15 vol.% glass filled polyethylene terephthalate (PET) using various recycling generations and recycled ratios were determined. Six recycling generations and 4 recycled ratios were used in this research. Calibration curves relating mechanical properties such as tensile strength, elastic modulus, and percent elongation to failure to the recycling generation or recycled ratios were developed. The calibration curves, which were generated, revealed that the properties of glass filled PET decreased slightly with recycling (2.1% to 5.1% per recycling generation). However, this slight decrease in properties can be compensated by conservative safety factors or plastics additives, as a result of which recycled plastics products can be manufactured without much concern about their mechanical performance. Thermal properties of the glass filled PET were not affected by the recycling process. In summary, recycling of plastic materials is effective in conserving the environment and enhancing the life cycle of these materials.

Resumen

Los plásticos reciclados son considerados materiales de baja calidad porque el desempeño en sus propiedades disminuye con el reciclaje. Los fabricantes de resina utilizan una simple regla al recomendar el uso de plásticos reciclados, usualmente 25% o menos por peso del peso total de la pieza. Esta regla asegura el desempeño de la pieza, pero es una regla conservadora y no está basada en experimentación.

El objetivo de esta investigación fue influir el cambio en la percepción de que los materiales plásticos son de baja calidad. Con este propósito, se determinaron las propiedades mecánicas de tereftalato de polietileno (PET) con 15% volumen de fibra de vidrio usando varias generaciones de reciclado y razón de material reciclado. Seis generaciones y 4 mezclas de plásticos virgen más reciclado y fueron utilizados en esta investigación. Para esto se generaron curvas de calibración relacionando las propiedades mecánicas tales como esfuerzo máximo de rompimiento, módulo de elasticidad y porcentaje de alargamiento de rompimiento con distintas mezclas entre plásticos reciclado y virgen y distintas generaciones. Las curvas de calibración que se generaron probaron que las propiedades del PET con fibra de vidrio disminuyen un poco con reciclaje (2.1% a 5.1% por generación de material reciclado). En cambio, esa pequeña disminución en propiedades podría ser compensado por los factores de seguridad conservativos o la adición de aditivo, como resultado de lo cual los productos de plásticos reciclados pueden ser manufacturados sin ninguna preocupación sobre su desempeño mecánico. Las propiedades térmicas del PET con fibra de vidrio no fueron afectadas por el proceso de reciclaje. En resumen, queda comprobado que el reciclaje de los materiales plásticos es efectivo en conservar en ambiente y mejorar el ciclo de vida de esos materiales.

Dedication

I dedicate this thesis to my family because they have given me the necessary support in all phases of my career. I dedicate it to my wife who helps me a lot with time distribution and entertaining our boy. Graciela, do not worry, the thesis is finished and now, we will spend more time together. Together we can work through all situations. I love you.

To my parents, who taught me that education is the future and provided me their support during my bachelor's degree and the first years of my master's degree. They supported me financially, with transportation and other tools, and in believing that you can do all that you propose. Here I am, finishing my master's degree. This is for you Dad.

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Chapter 1: Introduction and General Information

1.1 Introduction

Plastic materials are used widely in many consumer products. Plastics are used in low performance products like wrapping products, bottles, toys, and also high performance products like car components, bulletproof suits, and other products. Plastic materials have substituted ferrous, wood, and ceramic materials in many applications for which reason, plastic consumption has increased exponentially in the past decade. Until recently, plastic materials were disposed in landfills after their use. This disposal creates environmental and space problems because plastics are not very biodegradable and occupy a large volume. In Puerto Rico alone, each household produces 4.61 [1,2] waste pounds daily, of which 20% by weight are plastic materials (0.92 pounds).

To resolve environmental and space problems caused by plastic materials many countries have adopted a new management process, i.e., recycling. Recycling consists of processing post consumer materials to produce raw materials for new products. The recycling process has been in continuous improvement and today recyclers can produce plastic resins with 99.9% purity. However, the recycling process can change mechanical, physical, and chemical properties of plastic materials. This perception of change in properties results in recycled plastics having a low value and the tendency of industries to shun recycled materials because their performance may be affected.

Research of the property changes of recycled plastics is few and is not a frequently studied. Today some industries use the rule of thumb of using 25% or less of recycled scrap materials to produce new products. Many industries do not use post-consumer plastic materials, because they are considered low performance materials or it is lack of studies that show free-contaminants materials [3]. Although scientifically it has been proved that the recycling process affects the properties, these changes have not been quantified. This study was directed to quantifying the property change in plastic

materials, and finding clear tendencies to predict property changes as a result of the recycling process.

1.2 Problem

The plastic recycling industry is having tough times to find market for recycled material, because they are considered low performance materials and some markets are closed to recycled materials. For example, Federal Drug Administration (FDA) does not recommend recycled materials for direct contact with products, like is described by FDA [4] in: Guidance for Industry, Container Closure System for Packaging Human Drugs and Biologics. Besides, recycled materials cannot be used for any food container or chemical container.

A lot of research has been conducted to study container or bottle materials such as high-density polyethylene (HDPE) and PET [5, 6, 7, 8, 9]. However, specialty plastics and fiberglass-containing plastics have not been studied enough because only some companies use it, and if they are mixed with bottle plastics they may contaminate it and cause loss of their value in worldwide recycling markets [10]. Some companies, (for example Hewlett Packard [11] and Ford Motor Company) use fiberglass PET for consumer products and are developing some processes to use recycled plastics in new products. These companies need to understand material behavior to use recycled materials in new products, but this field is not well studied.

Cartridge material was analyzed because it is made of fiberglass PET, it is used for big scale consumer products, and cartridge manufacturing is leading efforts to use recycled materials in new products. For example, Hewlett-Packard (HP) operates a worldwide multi-phase recycling process where inkjet cartridges are recycled into raw materials including ferrous metal, precious metals, ink, and plastics [11]. HP is working to qualify recycled plastic outputs from the recycling program back into products. Two questions are required to enable closed-loop and closed-system recycling of plastic resins: (1) how do the material properties degrade over successive recycling generations, and (2) how do the material properties change with varying ratios of recycled to virgin resin. This research attempts to answer these questions and correlate material properties with respect to recycled content and recycling generation using PET filled with 15 vol.%

glass fibers, material used in Hewlett Packard cartridges [12]. The study also purports to generate calibration curves that will enable the prediction of material properties given different recycled content ratios and recycling generations. The key material properties to be evaluated include mechanical, thermal, and physical properties.

PET resin suppliers and molders have wide knowledge of the behavior of bottle plastics, but possess rather limited knowledge of other PET grades resins. HP operates a worldwide recycling process that generates non-bottle recycled PET and seeks information on recycled PET behavior. For this reason, this study is undertaken to determine the effect of recycling on the material properties of PET used in this research.

1.3 Objectives

Although the recycling industries have performed few similar researches during the past years, they have attempted to quantify or find tendencies to predict quality loss. For example, it has been shown in a recent study of recycled polycarbonate that rheological, thermal, and mechanical properties were only slightly inferior [13] than virgin materials. The above-mentioned research is most similar to the proposed research and demonstrates that polycarbonate with up to 15% or less of recycled material has properties similar to that of virgin material. This research work has the following objectives:

1. To study the properties of recycled materials to verify if they change due to the recycling process.
2. To verify if the changes in the properties of recycled materials are affected by the recycling process only or also by other factors.
3. To find clear tendencies in change to create calibration curves for recycled materials. These calibration curves will be used in predicting property change with the inclusion of post consumer recycled resin.
4. To verify if changes in properties are affected with plastic recycling generation.
5. To begin eliminating the use of rules of thumb to add recycled content in new product manufacturing.
6. To change manufacturer perception of recycled materials as low value materials and provide clear tendencies of the properties of recycled materials. Because resins producers do not recommend recycled materials usage.
7. To increase usage of recycled resins in new products.

This research creates calibration curves for property change with recycling to predict final properties. The property change prediction will help plastic manufacturing industries to have a clear direction to follow. When industries really understand the behavior of recycled materials, their opinion about these materials should change. The recycled materials can be widely used and will help to increase plastic recovery percent

because increasing knowledge about property change should increase the demand for recycled materials.

1.4 Polyethylene Terephthalate

Polyethylene terephthalate (PET or PETE) is a widely used thermoplastic, which is represented in polymer identification code with number 1 and belongs to the polyester family. PET is used in beverage containers; especially water, wrapping materials, toys, automobile components, fibers, inkjet cartridges, and other products.

Plastics materials which are polymers, are produced by a polymerization process. This process consists of joining one or more monomers (chemical compounds) to produce monomers-repeating chains. PET is produced by condensation polymerization. Condensation polymerization is accomplished by the combination of two monomers to produce the needed polymer and a small molecule, which is the by-product. This condensation polymerization reaction produces a repeating unit chain [14]. The polyester repeating unit is shown in Figure 1.

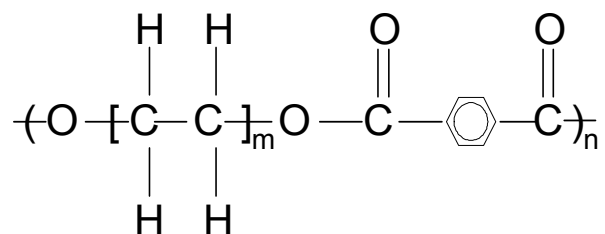


Figure 1: Polymer Repeating Unit for thermoplastic polyester

The m and n subscripts describe final material composition. If m=1, the final material is PET; if m=2, the final material is polybutylene terephthalate (PBT). Subscript n describes the amount of repeating units in a chain. Chain length and chains orientation gives polymer strength.

PET monomers are dimethyl terephthalate (DMA) and ethylene glycol, and the reaction by-product is water. Figure 2 shows the PET polymerization condensation reaction [15].

MWD is widely used to study polymer performance because it affects key properties like: melting temperature, tensile strength, and impact toughness. Some scientists consider that a material is a polymer if their molecular weight distribution is over 25,000 g/mol [15]. However, other factors affect material performance, namely, additives, entanglement of chains, and crystalline regions. Additives used commonly with plastics are lubricants, to minimize melted plastic viscosity, plasticizers, to increase material flow, and reinforcement fibers. Common reinforcement fibers are glass and carbon fiber [14,16].

For this research, 15% per weight glass filled PET with an average glass fiber length of 0.080 inches was used. Fiber reinforcement causes an increase in the mechanical properties. For example, non-reinforced PET has an average tensile strength of 50 MPa [17], compared with 150 MPa when PET is reinforced with 30% [17] of glass fiber; which is a 200% increase in tensile strength. In this research, the manufacturer-reported average tensile strength is about 100 MPa [12]. Fiber reinforcement depends on three main factors: fiber length, fiber diameter, and fiber material. Using the rule of mixtures (ROM), we can determine average fiber tensile strength. ROM explains that a mixture value is determined multiplying each material value by their respective ratios. The rule of mixtures is described by the following equation [14]:

$$P_{Mixture} = (P_{Fiber}) \times (R_{Fiber}) + (P_{Plastic}) \times (R_{Plastic}) \quad (1.1)$$

Using this equation, we determine that Glass Fiber Tensile Strength is:

$$100 \text{ MPa} = (TS_{Fiber}) \times (15\%) + (50 \text{ MPa}) \times (85\%)$$

$$TS_{Fiber} = 383 \text{ MPa}$$

Chain entanglement and crystalline regions also increase material performance. Chain entanglement can be explained with the spaghetti-plate-model. If long spaghettis are placed on a plate, and if one of these is moved, the other spaghettis will create a big resistance to flow [14]. On the other hand, if only short spaghettis are present and one of these short spaghettis is moved, there is less resistance to flow.

Crystalline regions are developed when chains align in certain polymer regions. These regions increase bonding force between chains, which increases overall material performance. PET polymer is a material inclined to crystallization because it has higher orientation effects [14]. These orientation effects are high for the polyester family. The molecules can be arranged randomly while cooling, but some processing methods are used to decrease orientation loss. Since the cartridge parts are cooled rapidly during molding process, orientation effects are present in the final part. See Figure 3 for more details.

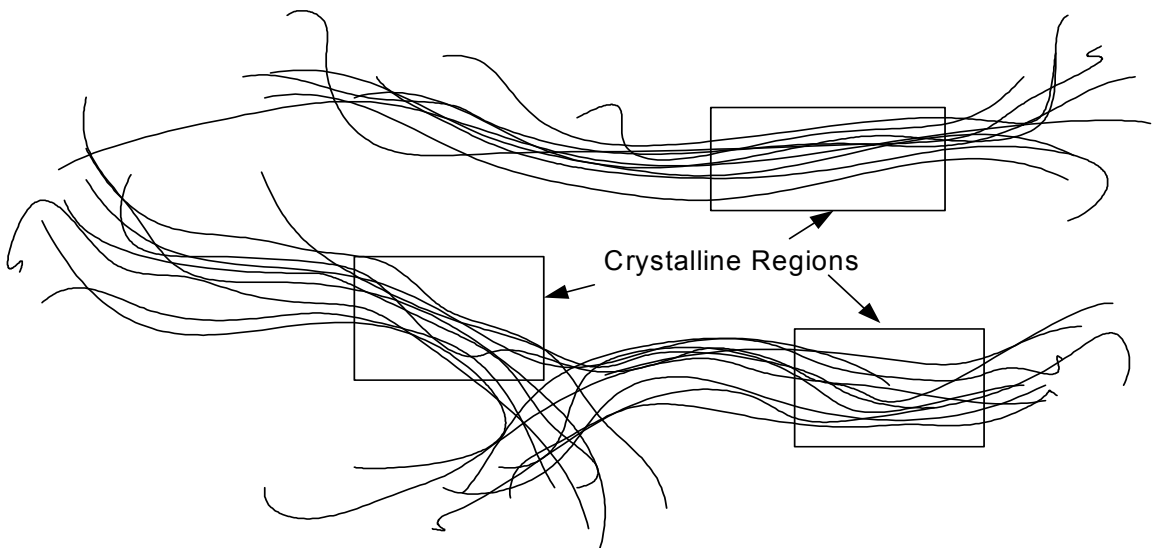


Figure 3: Schematic of Crystalline Regions in Polymers [18]

Chapter 2: Literature Revision

Studies in recycling content are few and difficult to find because the recycling industries are too young, and detailed scientific studies have not been conducted in this field. Recycling industries emerged in the middle 90s when landfill space problems began.

Historically, municipal waste has always been landfilled without any previous classification [5]. Plastic industries have increased exponentially [5] resulting in landfills being full of plastic materials. Some studies indicate that plastic materials occupy approximately double volume compared to weight percentage [5]. In Puerto Rico, the volume of plastics in landfills is nearly 23%. For plastics, the product life is very short, and the actual material has a useful life cycle of 1 month [5].

Plastic materials are a big problem in that they are reducing landfill space because of their low weight-volume ratio and slow biodegradability [5]. Polyethylene materials compose a great portion of plastic materials, but this material type is too difficult to use in injection molding applications [6] or extrusion applications because of its high viscosity. For this reason some manufacturers have mixed some recycled HDPE or PET to reduce the viscosity. The use of recycled resins to reduce viscosity is being studied and increases hopes in recycled material use. In some recent research, it has been proposed that 30% [6] or less of recycled materials can be used to reduce viscosity without significantly affecting material properties.

To increase the use of mixed materials it is necessary to add some compatibilisers to ensure material joining [6]. The mixed material cannot be used for food contact containers or chemical containers because it does not have the required stress cracking resistance [6]. Because recycled materials are assumed to have the poorest properties (although a lot of recent studies contradict this assumption) they are used predominantly

for low performance products like milk crates, mobile garage bins, traffic barricades, composts bins, [6] flowerpots, park benches, or plastic lumber. However, the low performance material conception has changed because some recent studies indicate results to the contrary. For example, it has been shown in a recent study of recycled polycarbonate that rheological, thermal, and mechanical properties were only slightly inferior [7] than virgin materials. The above-mentioned research is most similar to the proposed research and demonstrates that polycarbonate with up to 15% or less of recycled material has properties similar to that of virgin material. The proposed research is quite similar to the above study because the properties of recycled and virgin materials were measured for 0, 5, 15, 20, 50, and 100% by weight [13] along with glass transition temperature, viscosity, impact strength, and molecular weight distribution. The principal conclusions were that change in material properties is caused by complex viscosity. The complex viscosity can be caused by condensation polymerization [13]. This re-polymerization can be caused by high temperature generated in the processing steps during recycling [13].

Molecular weight distribution is used frequently to predict material properties. For example if a material has a high molecular weight distribution, the tensile modulus and viscosity will be high. The experience with recycled materials is that the higher molecular weight of the recycled polymer does not seem to affect the transition temperature [7]. In theory, transition temperature will be increased if the molecular weight increases. This particular behavior can be explained since recycled polycarbonate materials have complex viscosity caused because condensation polymerization reaction might occur during extrusion at a high temperature [7].

Additional investigation demonstrates that recycled materials are not low performance materials. For example, flexural properties of old recycled plastic lumber material, used during 11 years, increased with time [7]. This behavior is explained as the result of annealing [7]. The annealing process causes an increase in crystallinity, which induces a moderate increase in the mechanical properties [7]. This improvement in

properties is not affected by ultraviolet degradation because the recycled plastic lumber materials undergo surface degradation of only up to 0.003 inches per year [7]. Another important parameter to observe is that recycled plastic lumber material has low cost compared to wood materials when analyzed using life cost cycle analysis. For example, a forty year service life indicates that the cost of the wood structure is \$833 versus \$636 for recycled plastic lumber [7].

The increase in mechanical properties for recycled plastics was explained on the basis of a re-polymerization process. However, other research has contradicting results. For example, high density polyethylene (HDPE) is used for milk and juice containers, but is too viscous to be injection molded. In order to reduce viscosity, it is mixed with Injection Molding or Film Blowing grade HDPEs [8]. In this research, the properties improved because crosslinking between chains takes place, where this crosslinking behavior was noticed in melt flow index (MFI) plots [8]. The crosslinking causes crystallinity to be increased, thus improving properties.

Some additional procedures are being developed to use recycled materials for new products. Recycled glass filled nylon is produced in two separate material forms, fines, and heavies [17]. The different mixtures of heavies and fines materials can change material properties. For example, in this case, a change in glass fiber length causes a change in material properties where preliminary data shows a decrease in glass fiber length after being molded the first time [9].

In general, the perception that recycled material has low performance has not been corroborated with scientific studies [7, 13]. Recycled materials will be used for manufacturing new products because of minor involved costs [7] and because they are easier to process because of low viscosity. In many cases, the recycled plastic properties will be similar to or in some cases better than virgin material. Although, recycled plastic materials are considered as low performance materials, a clear and detailed analysis in property changes as a result of recycling can be quantified scientifically. A change in

perception is necessary because plastic materials occupy more than 20% of our landfills and this number is growing continually [5]. The recycled plastic materials market will expand, for which reason it is necessary to understand their behavior.

This research provides important data as to whether recycled plastics should be still considered as low performance materials because of property changes when recycled. The research also develops calibration curves that may be used to predict the properties of some virgin-recycled material mixtures. While previous research has studied some aspects of some recycled materials, the research presented studied the change in properties and finds clear tendencies to predict properties of recycled plastic materials.

Chapter 3: Methods

3.1 Preparation of Samples

3.1.1 Recycled Generation Samples

This study was carried out using 15% fiberglass polyethylene terephthalate (PET) produced by General Electric Plastics. The selected material, PET 15% fiberglass, is a composite material which contains 15% volume fraction of glass fibers mixed with PET resins. This PET material increases project complexity because the measured change in properties could be affected by fiber inclusion. The project scope is to produce samples for five different recycled generations (RG) and four different recycled ratios (RR).

3.1.2 Recycled-Virgin Mixture Samples

The selected materials are produced in Nypro Cayey molding production using a shredding and blending process. The project scope is to injection mold one-shot sample (16 pieces) per each recycled ratio and recycling generation. The recycled ratios (RR) used in this project were 0%, 25%, 50%, and 100%. Here 0% means virgin material, and 100% means completely recycled material. Material was recycled at least 5 times, for this reason research contains 0, 1st, 2nd, 3rd, 4th and 5th generations, where 0 corresponds to virgin material. Based on the manner in which the samples were produced continuously in Nypro facilities, resin purity is expected to be about 99.5%.

3.1.3 Samples Production and Nomenclature

In order to decrease product complexity, a special nomenclature was developed using ($A_x, B_y, \dots M_n$) layout. This layout describes any recycled-virgin resin mixture. The letters A, B, and M describe recycled generations present in the mixture and x, y and n subscripts describe recycled ratios. Recycled ratio numbers must always add up to 100%, for which reason $x + y + \dots + n = 1$. For example a mixture with 25% of virgin resin and 75%

of 2nd generation recycled resin is described as (0_{25,275}). A resin with 25% of 3rd generation recycled resin, 15% of 5th generation recycled resin, 30% of virgin material and 30% of 1st generation is described by: (0_{30,130,325,515}).

The samples for determining the mechanical and thermal properties were fabricated using injection molding and machining process. The part molded is known as side cover and can be observed in Figure 4. Side covers are used to maintain foam and other parts inside the inkjet cartridge. Inkjet cartridge that use PET side cover can be observed in Figure 5.



Figure 4: Side covers, used to produce test samples



Figure 5: Inkjet cartridge that use PET side covers.

The molding process was separated into two phases to minimize project complexity. All molding processes were conducted at Nypro Cayey facilities. The injection machine diagram is shown in Figure 6. Mixtures cannot be recycled again because they do not produce representative mixtures. For example, if a $(0_{25}, 3_{75})$ mixture is recycled, a $(1_{25}, 4_{75})$ mixture will result. This mixture is very difficult to produce in real life because manufactures do not know and cannot segregate recycling generation of post-consumer materials.

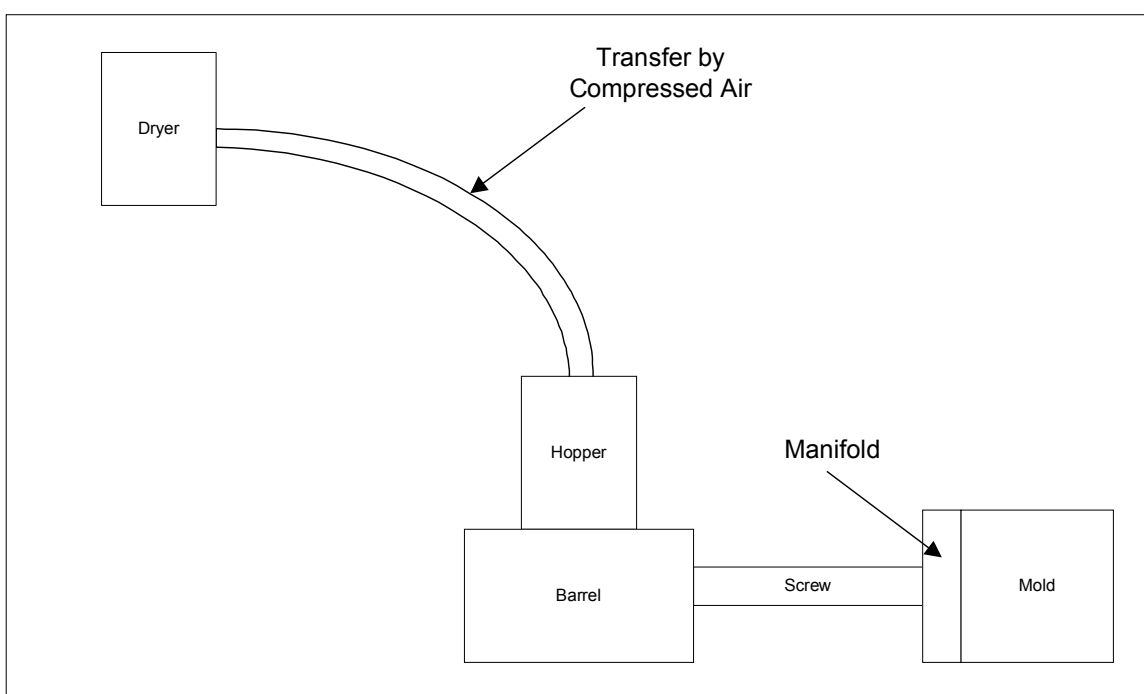


Figure 6: Injection Molding Diagram

Phase I –production of 100% samples.

1. Mold enough side covers with virgin PET material until process is stabilized. Nypro standard procedure shows that molding process stabilized after 10 shots. Before these 10 shots some particles could have contaminants like: other resins from prior molding process, over-heated material, or other materials. Each shot contain 16 side covers.

2. Take at least 5 side covers shots (40 bodies) to machine tension samples and run thermal tests.
3. Remaining molded side covers were shredded. The regrind material was molded again to produce 1st recycled generation sample.
4. Repeat steps 1 to 3 until samples for 1st, 2nd, 3rd, 4th, and 5th recycled generations are produced.

After Phase I, 30 samples were produced; 5 samples per each recycled generation, as is required by ASTM D638 [19]. Samples are described in Table 1:

Table 1: Samples produced in Phase I

Mixture	(0 ₁₀₀)	(0 ₀ ,1 ₁₀₀)	(0 ₀ ,2 ₁₀₀)	(0 ₀ ,3 ₁₀₀)	(0 ₀ ,4 ₁₀₀)	(0 ₀ ,5 ₁₀₀)	Total
QTY	5	5	5	5	5	5	30

Phase II –Production of virgin-recycled mixture. Produce different recycled ratio mixtures using virgin resin and different recycled generation resins.

The virgin and recycled material mixture is weighed before filling the machine hopper. The samples were fabricated using the following procedure:

1. Manually weigh the recycled and virgin resin.
2. Transfer to machine hopper the exact material quantity of virgin and recycled materials to produce the recycled ratio sample. (All recycled ratios were calculated using weight percent and loaded manually).
3. Flush all used resin to do the next recycled samples.
4. Select five shots (40 samples) to perform tests for each condition.
5. Repeat steps one to three with the next recycled content. The recycled contents and quantity of samples per material are described in Table 2.

Table 2: Samples produced in Phase II

Mixture	(0 ₇₅ ,1 ₂₅)	(0 ₅₀ ,1 ₅₀)	(0 ₇₅ ,2 ₂₅)	(0 ₅₀ ,2 ₅₀)	(0 ₇₅ ,3 ₂₅)	(0 ₅₀ ,3 ₅₀)	Total
QTY	5	5	5	5	5	5	30

In total 30 samples were generated. Samples description is shown in Table 3:

Table 3: Samples used in research

Recycled Generation	Recycled Ratio			
	0%	25%	50%	100%
0	(0 ₁₀₀)			
1	(0 ₁₀₀)	(0 ₇₅ ,1 ₂₅)	(0 ₅₀ ,1 ₅₀)	(0 ₀ ,1 ₁₀₀)
2		(0 ₇₅ ,2 ₂₅)	(0 ₅₀ ,2 ₅₀)	(0 ₀ ,2 ₁₀₀)
3		(0 ₇₅ ,3 ₂₅)	(0 ₅₀ ,3 ₅₀)	(0 ₀ ,3 ₁₀₀)
4		N/A		(0 ₀ ,4 ₁₀₀)
5		N/A		(0 ₀ ,5 ₁₀₀)

Samples for 4th and 5th generation using 25% and 50% of recycled resin were not produced to minimize research costs.

3.2 Mechanical Properties Evaluation

The samples to determine the mechanical properties were fabricated using the injection molding process (described in the previous section) followed by a machining process. ASTM standard D638 [19] was used to machine and test samples (see Figure 7). The side cover thickness is 0.01 inch. Hence Type I specimen was selected which can be used for specimens with thickness of 0.28 inch or less. Besides, Type I specimen is most used in flat materials.

The side covers were too small to machine tension samples that follow ASTM standards. The side covers only measure 2" in length, while ASTM standards require that they must measure 6", see Figure 7 for more details. For this reason, a reduction factor of 2.25 was used to produce new tension samples that fit within the side cover dimensions. ASTM and final tension sample dimensions are observed in Table 4.

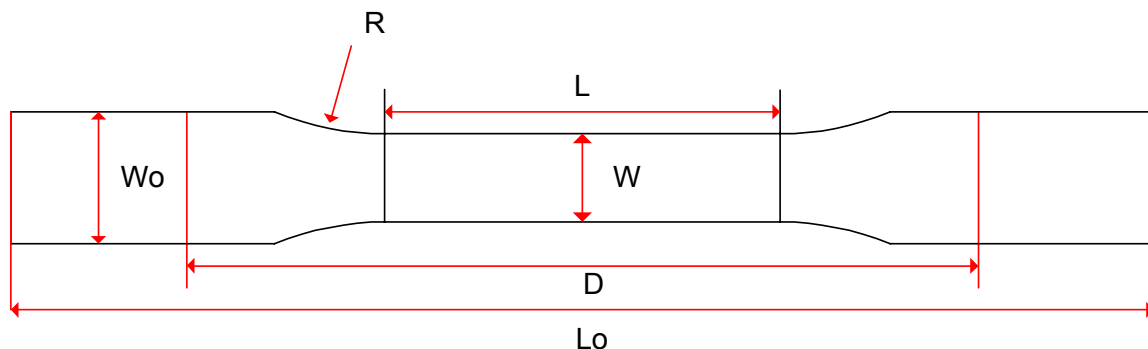


Figure 7: ASTM Tension Sample

Table 4: Comparison Table between ASTM and final sample dimensions

Description	ASTM (in.)	Final Tension Sample (in.)
W_o	$\frac{3}{4}$	$\frac{1}{3}$
R	3	$1 \frac{1}{3}$
L	2.25	1
W	$\frac{1}{2}$	$\frac{2}{9}$
D	$4 \frac{1}{2}$	2
L_o	$6 \frac{1}{2}$	$2 \frac{8}{9}$

Each sample was machined in the Hewlett Packard machine shop with a CNC machine. The machining program was developed by an equipment technician following the given tension specimen specifications. The cartridge side covers have ink channels that are used to guide ink to the bottom. These channels create stress concentration areas in the tension specimen causing premature breaking. To avoid this problem, each sample was machined (reduced) an additional 0.050" (0.127cm) in thickness.

Phase I samples were tested in an Instron machine 8872 located in the University of Puerto Rico, Mayagüez Campus, Mechanical Engineering Department. Tests were performed as per ASTM standard D638. The standard requires that the test velocity should be between $0.2 \pm 25\%$ and $2 \pm 10\%$ inch per minute for the Type I specimen. This velocity was specified for rigid or semi-rigid material. Also, the ASTM standard requires at least 5 samples to be tested for each experimental condition for the results to be valid. At least five tension samples were machined for each mixture; in total 150 or

more tension samples were machined. To measure strain during testing, a one-inch gage length strain gauge was used.

The initial tension tests did not produce valid results since the samples fractured at the specimen curvature (See Figure 8 for more details), in sections a or b. A closer examination of the tension samples indicated that the machining process created small grooves or notches in specimen, which acted as crack forming starters. These grooves were created by the CNC machine when it stops and changes direction. Valleys that measure less than 0.001inch create stress concentration areas in the specimen and coincided with the fractures in the radius of curvature of the machined specimens.

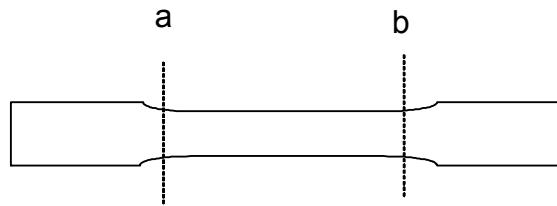


Figure 8: Premature breaking areas in tension specimen

To decrease stress concentration all the valleys in the specimens were eliminated by grinding manually with emery paper and checked to verify groove elimination using a magnifying glass.

Machined and ground specimens were used in Phase II. These samples were tested in the HP facility located in Corvallis, Oregon with an MTS Sintech 2/G machine because of calibration and hydraulic power problems with the Instron machine previously utilized. Phase II tension testing was carried out with the same parameters and no problems were encountered during this process.

Tension tests generated stress-strain diagrams. Figure 6 shows a schematic stress-strain diagram. From this stress-strain diagram three main properties can be read, ultimate tensile strength (UTS), elasticity modulus (E), and percent elongation to fracture (Elon. %.) Ultimate tensile strength is the material's ability to resist material flow, and is defined by:

$$\sigma = \text{Force} / \text{Area} \quad (3.2-1)$$

where F is the force measured by the testing machine and A is initial specimen cross sectional area.

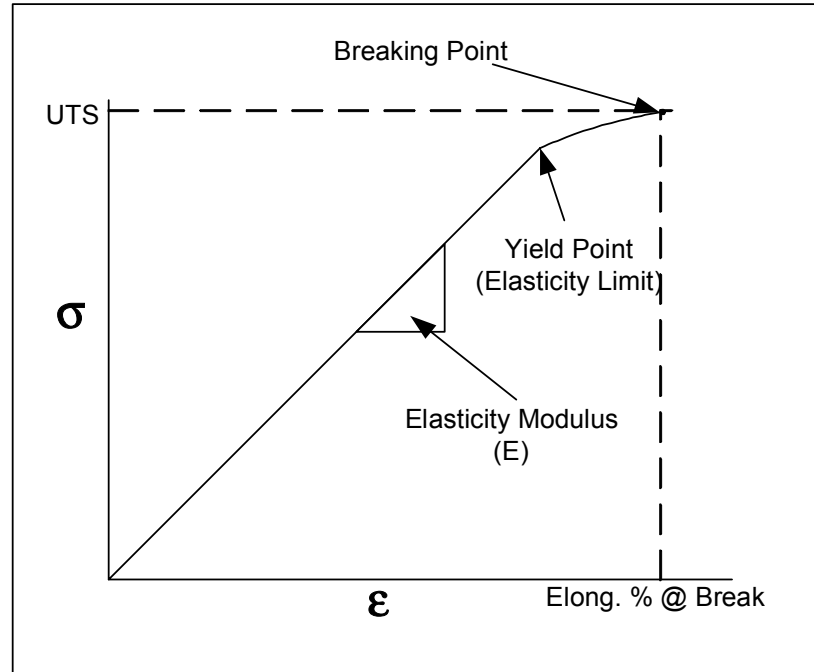


Figure 9: Typical Stress-Strain diagram

Elasticity modulus (E) is the rigidity of the material and resistance to elastic deformation. Elasticity modulus is the initial slope in stress-strain diagram, and is defined by:

$$E = \Delta\sigma / \Delta\epsilon \quad (3.2-2)$$

Where, $\Delta\sigma = \sigma_2 - \sigma_1$ is measured at any test between 0 point and yield point. Generally, stress is determined between 0 point and yield point. $\Delta\epsilon = L_f - L_i / L_i$, where L_f is the length at yield point and L_i is initial specimen length. Yield point is the point in the stress-strain diagram where there is a deviation from linear behavior.

Elongation percent refers to the elongation of the specimen during the test. Usually it is used for elongation to yield point, but in this research, it was determined at breaking point. Elongation percent is described by the following equation:

$$\text{Elon. \%} = L_f - L_i / L_i \times 100 \quad (3.2-3)$$

Where L_f is length at break and L_i is initial specimen length.

A stress-strain diagram was generated for each recycled content tension specimen (5 per each mixture) and compared with virgin material sample (see Appendix 2). Comparison plots were generated to see and understand recycled-virgin mixture properties, and in some cases, calibration curves were generated from this data, see results discussion chapter for more details.

To obtain valid mechanical property values, the criterion of 95% of t-student distribution was used. Values outside of this criterion were discarded and not used in analysis of the results.

3.3 Thermal Properties Evaluation

Recycled content bodies were analyzed with a Texas Instruments Differential Scanning Calorimeter (DSC) 2990 machine [20]. The DSC is used to determine thermal properties in polymers. Tests were performed at least three times to decrease measurement errors.

To measure thermal properties, 5 milligrams of sample for each recycled material body were taken. This 5-milligrams sample is put between two small discs. The pressed discs are then placed in the machine. The DSC performed the following steps to determine thermal properties:

1. Weigh specimen.
2. Apply heat and rotational movement to maintain homogenous heat in the sample.
3. Generate DSC thermogram

A typical thermogram can be observed in Figure 10, and describes thermal properties for polymers. It contains endothermic and exothermic regions, depending on chain reaction to heating. A thermogram may exhibit five primary regions: glass transition, crystallization, melting, crosslinking, and decomposition.

In the glass transition region, the polymer begins to heat up and absorb energy in the process. As a consequence, polymer chains begin to flow and the material loses hardness. Although, the polymer is in the solid state it flows very easily. Knowledge of the glass transition temperature is important in the design of plastics because it is the maximum temperature up to which plastic materials do not change their dimensions.

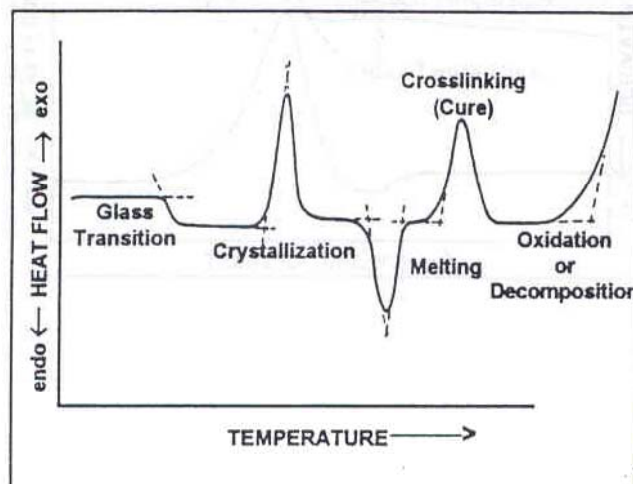


Figure 10: Typical DSC Thermogram

In the crystallization region, the polymer chains begin to misalign and lose heat (exothermic process) stored in their bonds. Once a polymer loses all its crystalline regions, it is 100% amorphous.

In the melting region, the polymer absorbs enormous amounts of energy causing that material to flow and change to the liquid state. A molten polymer is a non-Newtonian fluid with higher viscosity. The melting temperature is not a point but a distribution. Different chain lengths cause this distribution in melting temperature. Shorter chains flow faster than longer polymer chains causing this temperature difference. Molding processes use this temperature to determine processing temperatures. To minimize this temperature distribution effect during molding, melting temperature is not reached with heat only. Mechanical heat (heat caused by friction) also causes material to flow and avoid any molding problems, like overheating.

The main difference between thermoset and thermoplastics materials is the region of crosslinking regions. Thermoplastic materials possess no crosslinking regions. For thermosets, crosslinking region prevents material from flowing again, because the applied energy breaks both crosslinking and chains in the melting process. In the crosslinking region, cross-linked chains (chains that have bonds between them) lose this linking. Stored energy is released, causing an exothermic region. Crosslinking energy is too large, in some cases equal or higher than chain bonding energy. In Figure 10, the material has lower crosslinking energy compared to decomposition, although these values are very close.

The last region is the decomposition region. In this region, the chains break bonds and burn. This temperature is used in manufacturing process as an upper limit and never should be exceeded since this results in the loss of the final product.

The thermogram is used to determine different thermal properties like glass transition temperature (GT), melting temperature (MT), crystallinity percent (Crys. %), and crosslinking percent. The material analyzed in this research is a thermoplastic, for which reason crosslinking percent was not measured.

The melting temperature and glass transition temperature are generally reported as a distribution and not a unique value. Average values are used in this research because thermogram data was not available.

In polymers, crystalline regions are regions where chains are aligned, increasing mechanical properties principally. Crystallinity percent is a measure of the crystalline regions in the polymer. And crystalline percent is determined with the following equation.

$$\text{Cryst. \%} = \Delta E / c_{\text{PET}} \quad (3.3-1)$$

Where $\Delta E = E_m - E_c$. E_c is the amount of energy necessary to misalign crystalline regions in polymer, while, E_m is the amount of energy necessary to melt the polymer. c_{PET} is the specific heat of the polymer at constant volume (PET in this case).

Typical higher values for polymers are 15 to 18%. These values are low if similar processes that occur in metals are compared. Metals are mostly crystalline, but in

polymers a crystalline structure is not present. However, aligned chains have a similar effect in material properties as crystallinity in metals.

As in mechanical properties, 95% probability of t-student distribution was used to determine final thermal properties values. Values that did not meet this criterion were not included in the analysis.

Chapter 4: Results and Discussion

4.1 Mechanical Properties

The mechanical properties measured were Ultimate Tensile Strength (UTS), Elasticity Modulus (E), and Percent Elongation to Fracture (% Elong.) for different recycled-virgin material mixtures. Virgin PET material was recycled 5 times to have 1st, 2nd, 3rd, 4th, and 5th recycled generations (RG). These RGs were mixed with virgin material in 25:75, and 50:50 recycled ratios (RR). 4th and 5th RG materials were not mixed with virgin material to reduce project complexity and costs.

4.1.1 Different Recycled Generations

Six different RGs were used in this research. For each one, at least five tension specimens were machined and tested. Traditional theory explains that recycled materials should possess poor mechanical properties compared to virgin material, but few studies have measured these differences. Calibration curves were generated for UTS and Elasticity Modulus which describes experimental behavior.

4.1.1.1 Ultimate Tensile Strength

The results are summarized in Table 5 for each recycled generation. In total only 8 values were outside the 95% probability criterion. Details about standard deviation and elimination process can be referred to in Appendix # 1. However, a decreasing trend is observed in the average values of UTS for the recycled process samples.

Table 5: Summarized UTS data for 100% PET RC Samples

RG(100% RC)	Ultimate Tensile Strength (MPa)					
	1	2	3	4	5	Average
(0 ₁₀₀)	63.94	70.43*	45.87*	59.9	57.29	59.486
(0 _{0,100})	41.51*	68.56*	55.07	55.72	54.11	54.991
(0 _{0,200})	54.96	64.14*	52.81	58.80	48.23*	55.787
(0 _{0,300})	54.39	56.00	55.11	54.45	55.65	55.119
(0 _{0,400})	35.41*	46.17	47.13	50.56	46.36	45.126
(0 _{0,500})	40.65	49.06	53.24*	43.27	40.14	45.270

* Values outside 95% probability t-student distribution

Different constituents like fillers fiber length, glass and carbon fiber, lubricants, colorants, chain length, crosslinking presence, re-constituents, and other additives affect mechanical properties in plastics improving or decreasing. Re-constituents are additives designed to improve mechanical properties and they are added during molding process.

In this research, it was assumed that the materials do not exhibit lubricants and colorants losses. This was assumed because it is very difficult to quantify and measure lubricant and colorant loses, and effect in mechanical properties could be zero. Crosslinking was not exhibited because the material melted for all RG, RR, and re-constituents were not added. For this reason only three main factors could affect mechanical properties glass fiber content, chain length shortening and crystallinity percent change.

The decreasing trend is caused by three different factors at the same time, glass fiber shortening, chain length decreasing, and crystallinity percent increasing inside PET material. Recycled materials were ground and molded more than one time. This process causes that glass fiber effective length, chain length decrease, and mechanical properties, like UTS, to decrease too. However, crystallinity percent stabilized and increased after 5th generation (Detailed information on why crystallinity percent increased can be found in Chapter 4.2.3). Crys. % causes mechanical properties to increase. In this case, UTS decreased during the first two generations because fiber length and crystallinity percent decreased in the same RG. However, UTS stabilized from 1st to 3rd recycled generation because crystallinity percent compensates fiber length shortage. In 4th and 5th RG, crystallinity percent increasing is not sufficient and fiber length decrease mechanical properties. This trend can be observed in Figure #8.

After eliminating values, which lie outside the required criterion, new average values were determined. These are given in Table 6.

Table 6: Average UTS values before and after 95% probability criteria.

Average UTS (MPa)		
RG	Before	After
0	59.486	60.375
1	54.991	54.964
2	55.787	55.522
3	55.119	55.119
4	45.126	47.555
5	45.270	43.277

Average values show decreasing behavior of UTS that can be observed in Figure 11. Experimental points show good fit when compared with linear regression with an r-squared value of 0.8803. Table 7 compares the data points with the regression, and the maximum difference between average and linear approximation is 6.57%.

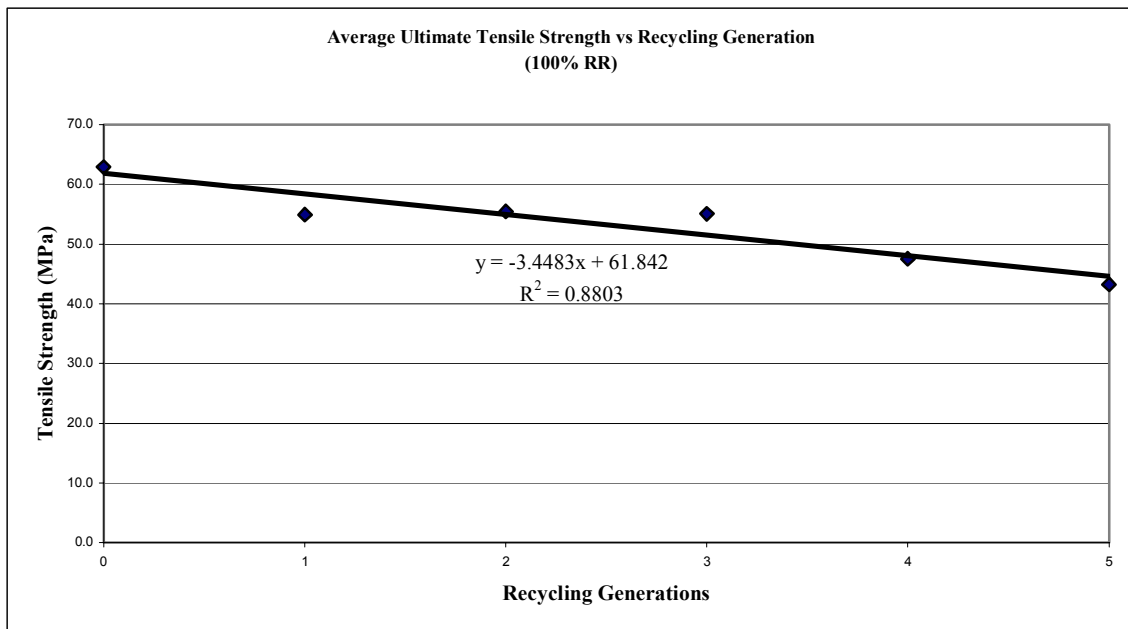
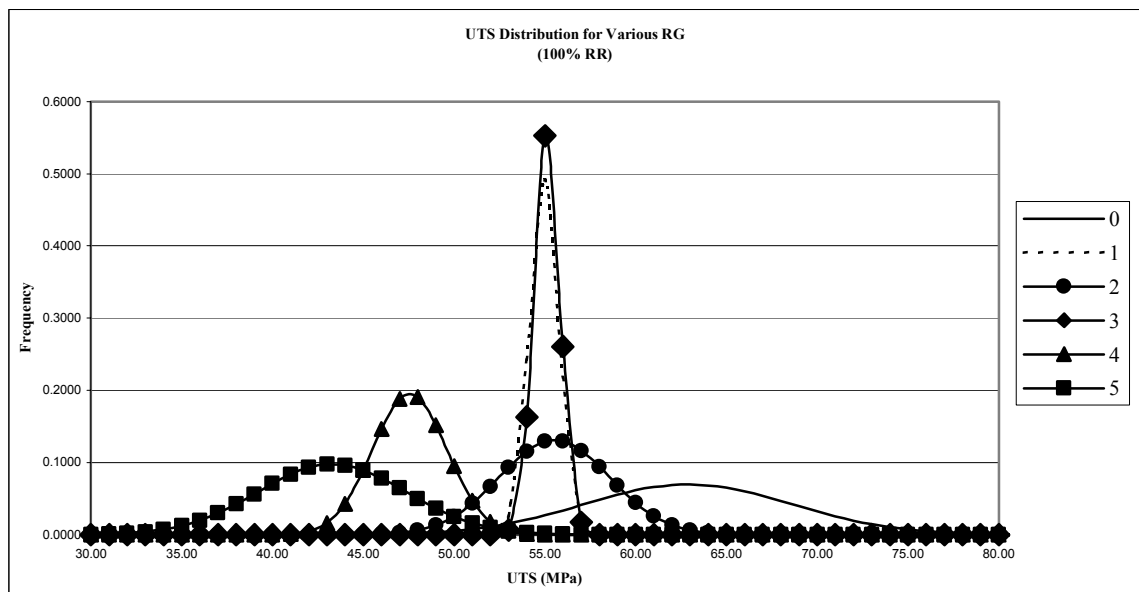
**Figure 11: UTS lineal regression for 100% RR and different generations**

Table 7: Comparison of average and curve fitted values of UTS

Sample	Average UTS (MPa)	UTS Based on Linear Fit	Diff %
(0 ₁₀₀)	60.375	61.842	1.67%
(0 ₀ ,1 ₁₀₀)	54.964	58.393	6.24%
(0 ₀ ,2 ₁₀₀)	55.522	54.945	1.04%
(0 ₀ ,3 ₁₀₀)	55.119	51.497	6.57%
(0 ₀ ,4 ₁₀₀)	47.555	48.048	1.04%
(0 ₀ ,5 ₁₀₀)	43.277	44.600	3.06%

Using linear fit, an average UTS loss is calculated to be about 5.6 % (see Figure 11 for more details) per each recycling generation. These are small losses considering that these are 100% RR. This effect is caused principally by fiber shortening.

The effect of recycled material in the range of distribution of properties was also considered. Observing Figure 12, unmixed material has a broad distribution as a result of which a change in average UTS cannot be observed after the 3rd generation.

**Figure 12: UTS Distribution for 100%RR**

From virgin material to 3rd generation, property distribution is narrow and average UTS remains constant (1st to 3rd RG). However, after the 3rd generation average UTS decreases and distribution does not follow a clearly defined behavior. PET material has a

broad UTS distribution; this means that has it many long and shorter chains and/or fibers. Chain length was not measured, but thermal properties behavior show that it does not change. UTS distribution shows that it longer fibers are cut first than shorter fibers. For this reason, until all fibers are cut, the distribution has similar width during 1st to 3rd RG. After 4th RG fibers have similar length, and additional fiber shortage causes lower average values and broader distributions.

4.1.1.2 Elasticity Modulus

The elasticity modulus was determined for each recycled generation. The process to determine elasticity modulus can be observed in Appendix # 1. Tabulated results can be observed in Table 8, and average values were determined after eliminating outliers outside the 95% probability of t-student distribution.

Table 8: Summarized Elasticity Modulus data for 100% RC

RG (100% RC)	Elasticity Modulus (GPa)					
	1	2	3	4	5	Average
(0 ₁₀₀)	3.506*	4.288	4.716	4.065	4.679	3.506
(0 _{0,1} 100)	4.122	0.000 ⁺	4.114	3.675*	3.925	4.122
(0 _{0,2} 100)	3.928	4.000	3.732*	3.800	3.965	3.928
(0 _{0,3} 100)	3.828	3.773	3.732	3.703	3.555*	3.828
(0 _{0,4} 100)	3.524*	3.894	3.926	3.674	3.681	3.524
(0 _{0,5} 100)	3.458	3.804	3.758	3.429	3.844	3.458

* Values outside 95% probability t-student distribution

⁺ Processing error (Strain gauge was not used)

After eliminating values, which are outliers, new average values were determined which are given in Table 9.

Table 9: Average E values of before and after 95% probability criteria.

Average E (GPa)	
Old	New
5.314	4.437
5.279	4.054
4.856	3.923
4.648	3.759
4.675	3.794
3.659	3.659

Average values indicate a decreasing trend of the elasticity modulus with recycled generation, which can be observed in Figure 13. Experimental points were compared with linear regression and produce a good fit with r-squared value of 0.8488. Comparing experimental points with linear regression, the maximum difference between average and linear approximation is 3.47%.

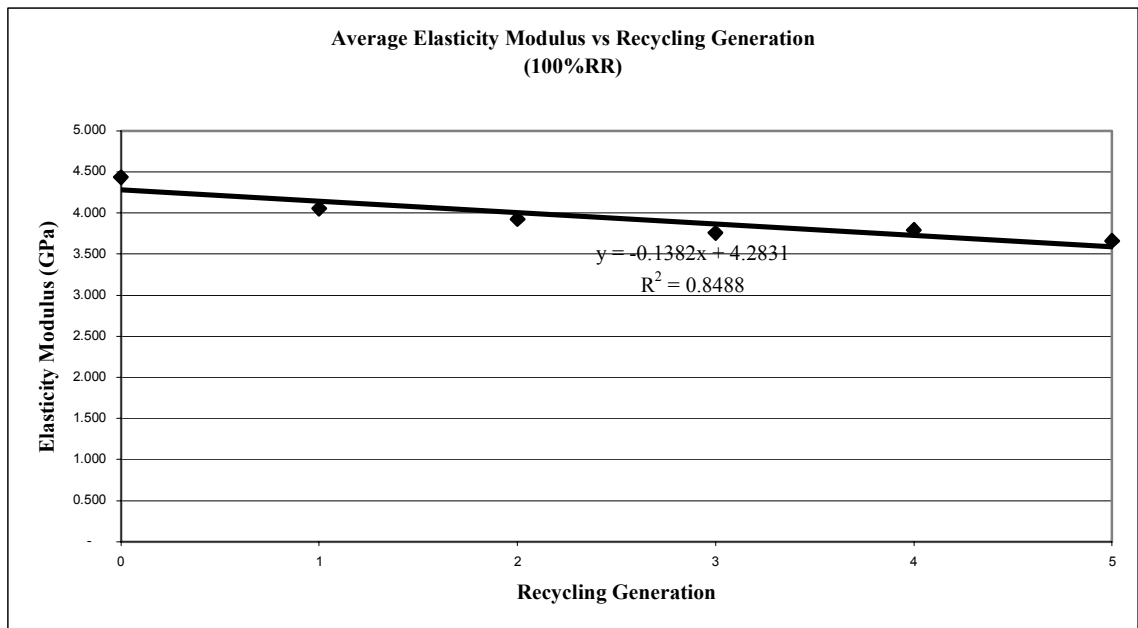


Figure 13: Elasticity Modulus linear regression for 100% RR and different generations

Table 10: Comparison of average and curve fitted values of E for 100 RR

Sample	Average UTS (MPa)	UTS Based on Lineal Fit	Diff %
(0 ₁₀₀)	60.375	61.842	1.67%
(0 _{0,1} ₁₀₀)	54.964	58.393	6.24%
(0 _{0,2} ₁₀₀)	55.522	54.945	1.04%
(0 _{0,3} ₁₀₀)	55.119	51.497	6.57%
(0 _{0,4} ₁₀₀)	47.555	48.048	1.04%
(0 _{0,5} ₁₀₀)	43.277	44.600	3.06%

Using linear fit (see Table 10), the average UTS loss is about 3.2 % per each recycling generation (see Figure 13 for more details). These, again, are small losses considering that these materials are 100% RR. Again, E losses are due by combined factors, chain and fiber length vs. crystallinity percent. Since chains length should remain constant, (see Chapter 4.2) only fiber and crystallinity percent change cause mechanical properties change. Thermal properties do not change (see Chapter 4.2 for more details), this means that chain length remain constant.

E decrease from 0 to 1st RG, remain constant during 1st to 3rd RG and decreases after 4th RG. Since UTS, this effect is caused because fiber length decreases mechanical properties, but crystallinity percent increases. In the plateau, RG 1 to 3, crystallinity percent effect compensates fiber length effect. But, after 4th RG fiber length decrease is not compensated by crystallinity percent and E decrease.

The effect of recycled material in the range of distribution of elasticity modulus was analyzed. Observing Figure 14, virgin elasticity modulus distribution is broad compared with different recycling generation. Average elasticity modulus follows decreasing behavior, and average distribution remains constant from 1st to 4th generation.

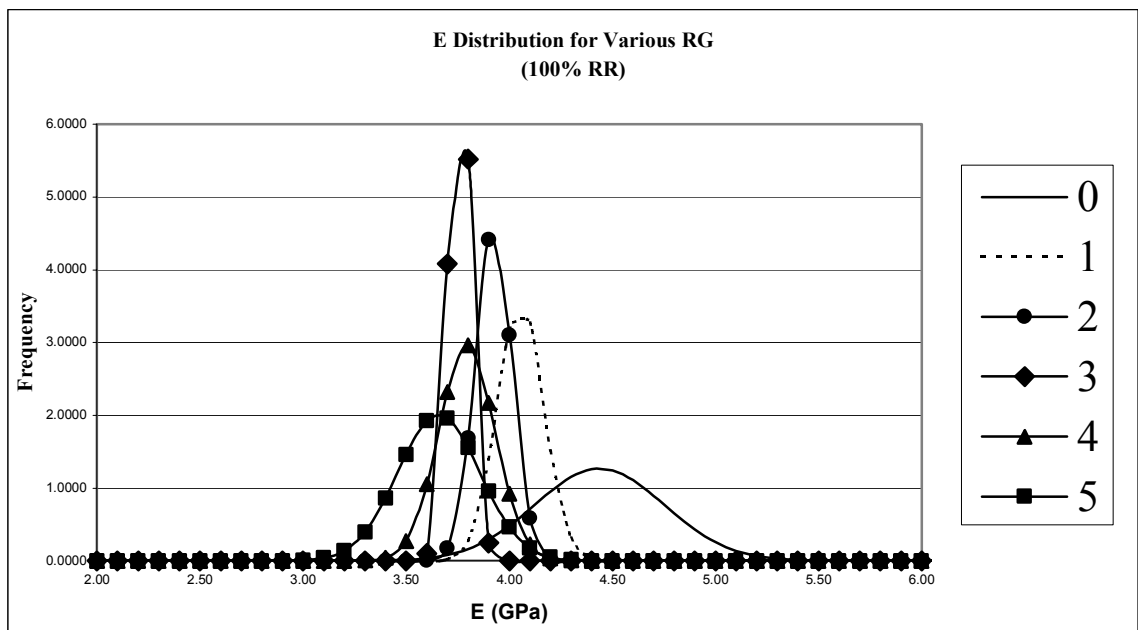


Figure 14: E Distribution for 100%RR

After the 4th generation, elasticity modulus distribution is broader than previous generations. The distribution follows same trends as UTS variation. Distribution has similar widths while longer and shorter fibers are cut; besides average values decrease. Distribution width increasing means more variability in fiber lengths.

4.1.1.3 Elongation Percent

Elongation percent was also determined for each recycling generation. Elongation percent values can be observed in Table 11, and they do not indicate any particular trend. The same 95%-probability of t-student distribution criterion was used to eliminate values. Despite this exercise, a clear tendency was not observed. Average values before and after eliminating far values can be observed in Table 12 and do not follow any clear tendency.

Table 11: Summarized Elongation Percent data for 100% RC

RG (100% RC)	Elongation Percent					
	1	2	3	4	5	Average
(0 ₁₀₀)	1.823	2.274*	0.972*	1.470	1.415	1.569
(0 _{0,1} ₁₀₀)	1.105	0.000*	1.537	1.668	1.303	1.403
(0 _{0,2} ₁₀₀)	1.796	2.021	1.452	1.125	3.040*	1.599
(0 _{0,3} ₁₀₀)	1.667	3.599*	1.666	1.639	1.864	1.709
(0 _{0,4} ₁₀₀)	1.082*	1.330	1.280	1.482*	1.251	1.287
(0 _{0,5} ₁₀₀)	1.290	1.492	1.594	1.478	1.044*	1.464

* Values outside 95% probability t-student distribution

Table 12: Average Elon. % values before and after 95% probability criteria.

Average Elon. %	
Old	New
1.569	1.591
1.403	1.123
1.599	1.887
1.709	2.087
1.287	1.285
1.464	1.380

Elongation percent does not exhibit any clear behavior with RG change due to glass fiber inclusion. Follows rules of mixtures, a material elongates until strong material elongates. Glass fiber dominates elongation percent, and it does not exhibit any clear behavior because fiber lengths change with RG.

Experimental values do not show any particular tendency, for which reason a valid regression analysis could not be carried out. Also, the distributions for these values follow different tendencies. Figure 15 shows that elongation percent distributions have different widths and do not follow any behavior. All values are between 1% and 2% and the average elongation is 1.464 ± 0.298 %.

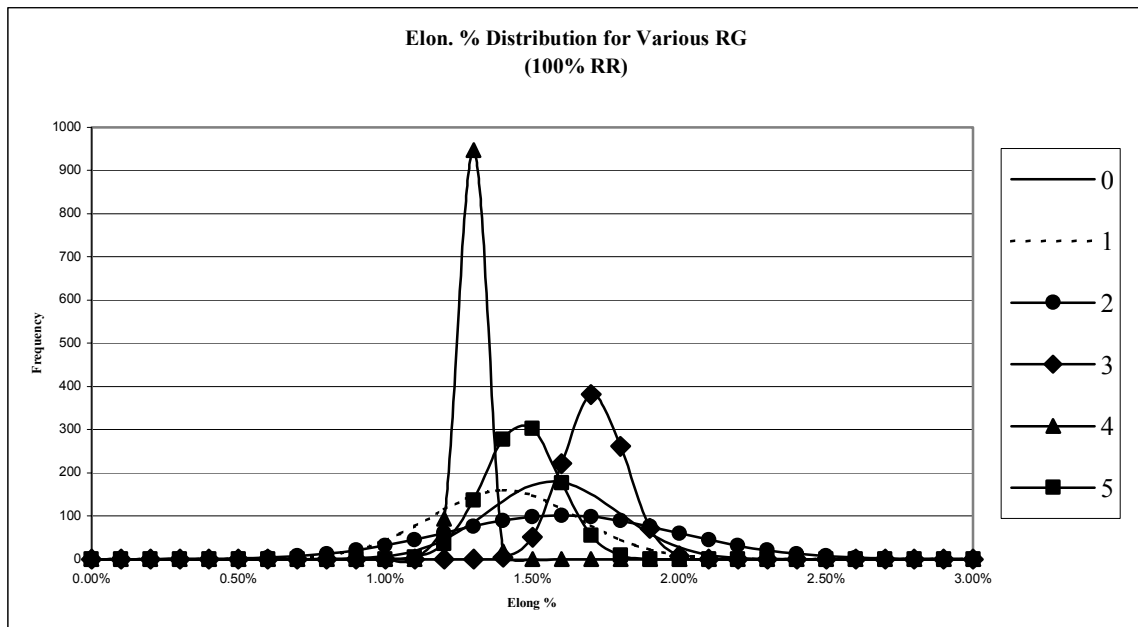


Figure 15: Elong % Distribution for 100%RR

4.1.2 Different Recycled Ratios

Samples tested in Phase II will be explained in the following section. These samples contain different recycling generation in different recycling ratios, 100-0, 75-25, 50-50, and 0-100. Calibration curves were not generated because only a few data points were obtained (only 2 per generation). Tension tests were performed at least 5 times per condition following the ASTM standard.

4.1.2.1 Ultimate Tensile Strength

Ultimate tensile strength was determined from 5 tests following the ASTM standard. Using the 95%-probability of t-student distribution criteria, average values were determined. Regression models and distribution plots could not be generated because only 2 points per generation were obtained, but decreasing behavior can be observed with values in the same recycling generation. Table 13 shows experimental UTS values. In addition, Table 14 shows average values before and after eliminating values outside of t-student distribution.

Table 13: Summarized UTS data for different % RR and RG

Sample Description		Ultimate Tensile Strength (MPa)					Average
RG	%RR	1	2	3	4	5	
1	25%	61.125	62.565	62.441	62.972	61.954	62.211
1	50%	57.340*	51.086	59.350	58.489	0.000*	45.253
2	25%	63.970	54.862*	66.752	58.166	62.384	61.227
2	50%	56.443	56.565	62.013	49.768*	58.779	56.713
3	25%	61.441*	57.902	57.690	54.401	56.186	57.524
3	50%	63.707	52.841*	63.441	64.607	58.922	60.703

* Values outside 95% probability t-student distribution

Table 14: Average UTS values before and after 95% probability criteria.

Average UTS (MPa)	
Before	After
62.211	62.211
45.253	58.393
61.227	62.818
56.713	58.450
57.524	56.545
60.703	62.669

4.1.2.2 Elasticity Modulus

Elasticity modulus was determined for 5 samples following the ASTM standard D638. Using the 95%-probability of t-student distribution elimination criterion, average

values were determined. Regression models and distribution plots could not be generated because of few data points that were available. However, a decreasing trend can be observed for values within the same recycling generation. Table 15 shows experimental UTS values. In addition, Table 16 shows average values before and after use of the elimination criterion.

Table 15: Summarized E data for different % RC and RG

Sample Description		Elasticity Modulus (GPa)					Average
RG	%RR	1	2	3	4	5	
1	25%	4.230	4.057	4.203	4.277	3.953	4.144
1	50%	4.078	3.364*	3.672	4.003	0.000*	3.023
2	25%	4.093	3.591	3.831	3.375*	3.987	3.776
2	50%	3.810	4.184	3.959	4.170	3.908	4.006
3	25%	3.966	4.345	4.213	3.807*	4.308	4.128
3	50%	3.141*	4.524*	4.041	3.927	3.743	3.875

Table 16: Average E values before and after 95% probability criteria.

Average E (GPa)	
Before	After
4.144	4.144
3.023	3.917
3.776	3.876
4.006	4.006
4.128	4.208
3.875	3.904

4.1.2.3 Elongation Percent

Elongation percent was also determined for 5 samples following the ASTM standard D638. After the 95%-probability of t-student distribution was used to eliminate outliers, average values were determined. Although regression models and distribution plots were not generated because of the lack of many data points, a decreasing trend can be observed for values in the same recycling generation. Table 17 shows experimental elongation values. In addition, Table 18 shows average values before and after eliminating outliers.

Table 17: Summarized Elon. % data for different % RC and RG

Samples Description		Elasticity Modulus (GPa)					Average
RG	%RR	1	2	3	4	5	
1	25%	1.664	1.729	1.680	1.664	1.732	1.694
1	50%	1.483	1.603	1.762	1.596	0.000	1.611
2	25%	1.683	1.592	1.827	1.879	1.692	1.735
2	50%	1.607	1.458	1.723	1.223	1.665	1.535
3	25%	1.618	1.512	1.422	1.496	1.419	1.493
3	50%	1.776	1.310	1.766	1.820	1.710	1.676

Table 18: Average Elon. % values before and after 95% probability criteria.

Average Elon. %	
Before	After
1.694	1.694
1.289	1.561
1.735	1.699
1.535	1.613
1.493	1.462
1.676	1.768

4.1.3 General Findings and Behaviors

To measure decrease in properties with the inclusion of recycled material, it was necessary to include Phase I and Phase II samples. Average property values, calculated after discarding outlier data points, were used for analysis. Properties tend to degrade with recycled material inclusion for UTS and E. In some cases, regression models were generated and calibration equations were determined. Three main calibration curves were generated:

1. Effect of recycling generation on material properties
2. Effect of recycled ratio on material properties
3. Combined effect using a 3-D curve

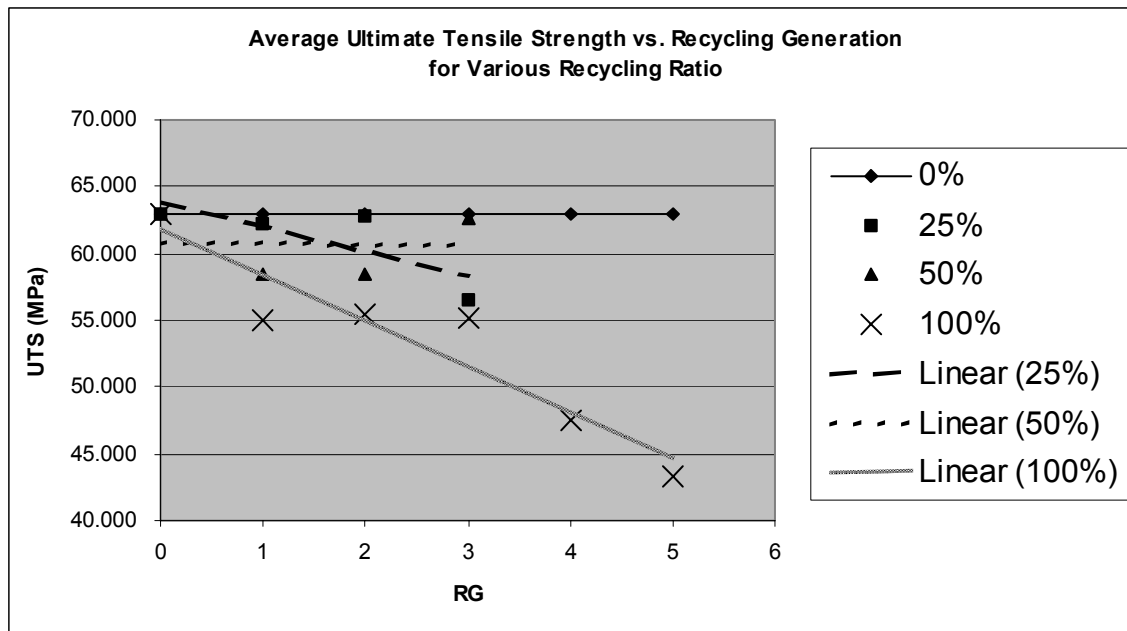
4.1.3.1 Ultimate Tensile Strength

Ultimate tensile strength follows a decreasing tendency with RG and RR. Final average values can be observed in Table 19. Using these values calibration and distribution curves were generated.

Table 19: Average UTS values for different RG and RR.

		Recycling Ratio			
		0%	25%	50%	100%
Recycling Generations	0	62.889	62.889	62.889	62.889
	1	62.889	62.211	58.393	54.964
	2	62.889	62.818	58.450	55.522
	3	62.889	56.545	62.669	55.119
	4	62.889	N/A		47.555
	5	62.889			43.277

UTS decreases with recycling generation. Linear regression was developed for each recycling ratio and Figure 16 shows this tendency. For 100% recycled ratio, a linear regression was developed in section 4.1.1 with a good fit because the r-squared value is 0.880. Linear regressions for 25% and 50% do not indicate a good fit because r-squared values are 0.603 and 0.001 respectively. These poor fits can be caused by the absence of experimental data, 4 points for 25% and 50% versus 6 points for 100%. In 100% RR-regression, UTS decreases from virgin to 1st RG, remains constant from 1st to 3rd RG, and decreases again from 4th to 5th RG. This behavior cannot be observed in 25% and 50% RR samples because 4th and 5th RG samples were not manufactured.

**Figure 16: Linear regression for different RR and different generations**

Comparison between linear regressions and experimental values can be observed in Table 20. Linear regression has a good fit for 25% and 100% RR with a maximum difference of 6.57%. Meanwhile, linear regression does not indicate a good fit for 50% RR, although the maximum difference was 3.83%. Experimental values for 50%RR remain constant with a distribution of 60.6 ± 3.12 MPa.

Table 20: Experimental and Linear Fit Comparison for different RR

RG	RR	Experimental	Linear Fit	Difference
0	25%	62.889	63.880	1.58%
1		62.211	62.037	0.28%
2		62.818	60.194	4.18%
3		56.545	58.351	3.20%
0	50%	62.889	60.691	3.50%
1		58.393	60.630	3.83%
2		58.450	60.570	3.63%
3		62.669	60.509	3.45%
0	100%	62.889	61.840	1.67%
1		54.964	58.393	6.24%
2		55.522	54.945	1.04%
3		55.119	51.497	6.57%
4		47.555	48.048	1.04%
5		43.277	44.600	3.06%

Experimental points in Figure 14 show that UTS decreases with RR. Linear regression has a good fit for 1st and 2nd generation because r-squared values are 0.958 and 0.918 respectively. Decreasing behavior can be observed for the 3rd generation also, but linear regression does not fit well with experimental values. Comparing linear regression with experimental values the maximum difference is only 7.7%. Table 21 compares experimental and linear fit for different RRs.

UTS behavior with different RR has similar trend that UTS with different RG, that is, both decrease. But, in the former, UTS decreases, from virgin to 100 % RR lineally. The RR samples have better properties than RG samples because virgin material addition adds fibers that improve mechanical properties. Comparing different UTS with same RR but different RG reveals a small decrease. RR inclusion dilutes mechanical properties losses, but again a plateau can be observed. Comparison of average losses

between same RR and different RG shows that UTS decreases more in 1st RG than 2nd and 3rd RG. This follows same trends that RG, decrease in 1st RG but remain constant from 2nd to 3rd.

Table 21: Experimental and Linear Fit Comparison for different RGs

RR	RG	Experimental	Linear Fit	Difference
0%	1	62.889	62.492	0.63%
25%		60.830	60.465	0.60%
50%		57.095	58.438	2.35%
100%		54.964	54.384	1.06%
0%	2	62.889	62.629	0.41%
25%		61.423	60.696	1.18%
50%		57.152	58.764	2.82%
100%		55.522	54.898	1.12%
0%	3	62.889	60.954	3.08%
25%		55.288	59.543	7.70%
50%		60.645	58.132	4.14%
100%		55.119	55.311	0.35%

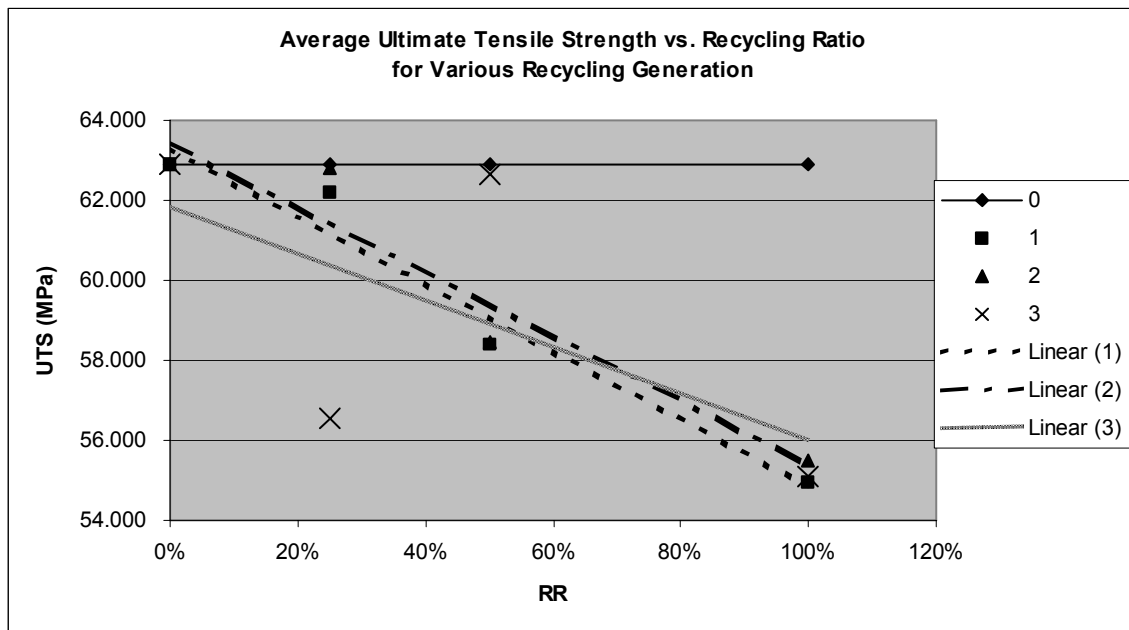


Figure 17: Linear regression for different RG and different ratios.

UTS distributions for different RRs at same RG follow the same tendency as that for 100% RR. Average values decrease with RG during the first generation and remain

constant in 2nd and 3rd RG. Distribution for 1st generation and 25% RR is narrower than for virgin material, but 2nd and 3rd generations have the same width as the distribution virgin material. This effect can be observed in Figure 18.

Again, the fiber length causes this effect. Virgin material has many long and shorter fibers. Recycling process begin to cut longer fibers, and later shorter ones. For his reason average value remain constant, but distribution is fine. Average value decrease after 3rd RG, because all fibers have being cut at the same rate causing UTS decreasing. Same behavior is exhibit with 25% and 50% of RR.

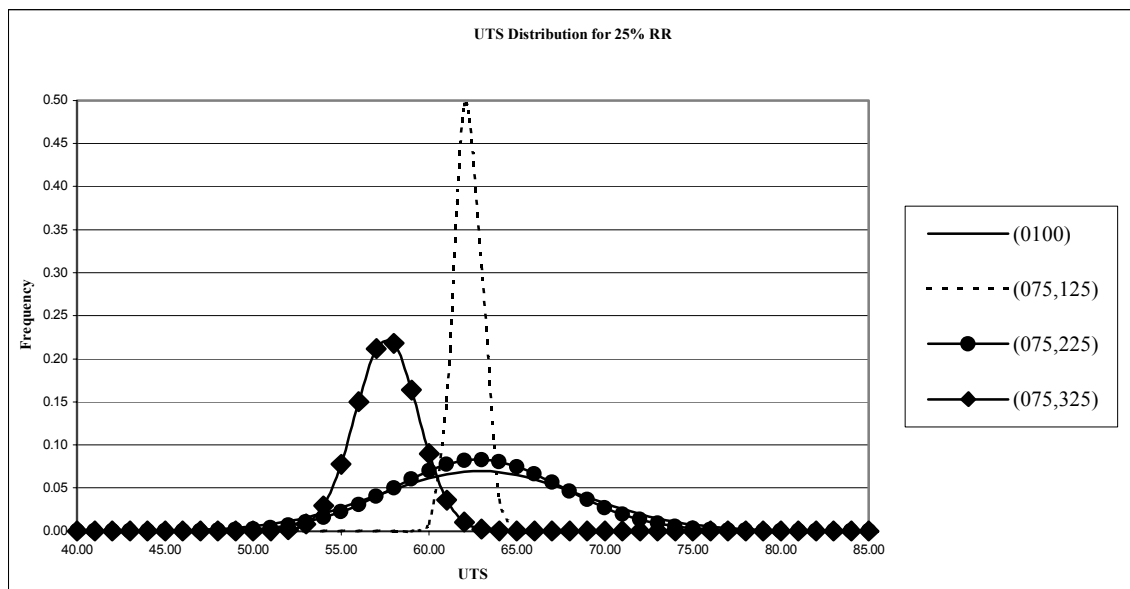


Figure 18: UTS Distribution for 25%RR

The distribution for the 2nd generation has a similar tendency, with the 1st generation distribution being narrower than for virgin material, and 2nd and 3rd generation having similar width as the virgin samples. Figure 19 shows this behavior. The decrease in average UTS, for RR 25% and 50%, from one RG to the other is not too great because small percents are not enough to observe big changes.

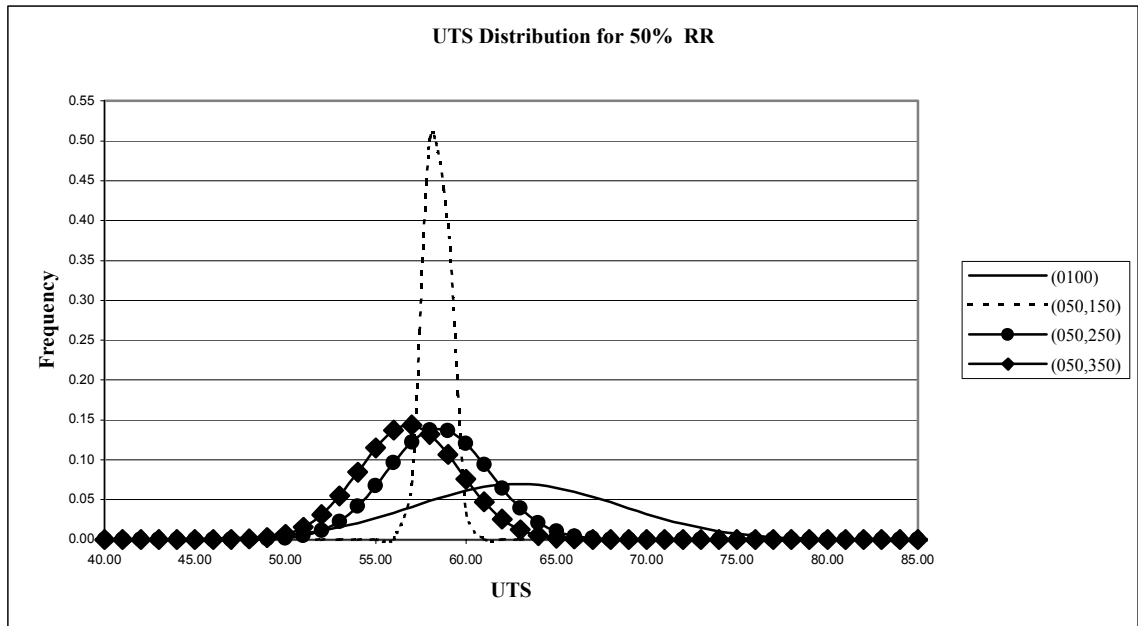


Figure 19: UTS Distribution for 50%RR

4.1.3.2 Elasticity Modulus

Elasticity Modulus follows a decreasing tendency with RG and RR. Final average values can be observed in Table 22. Using these values, calibration and distribution curves were generated.

Table 22: Average E values for different RG and RR

		Recycling Ratio			
		0%	25%	50%	100%
Recycling Generation	0	4.437	4.437	4.437	4.437
	1	4.437	4.144	3.917	4.054
	2	4.437	3.876	4.006	3.923
	3	4.437	4.208	3.904	3.759
	4	4.437	N/A		3.794
	5	4.437			3.659

E decreases with recycling generation and this tendency is seen in Figure 20. Lineal regression was developed for each recycling ratio. For 100% recycled ratio, linear regression analysis was carried out in section 4.1.2. Linear regression shows good fit because r-squared value is 0.849. On the other hand, linear regression for 25% and 50% does not show good fit because r-squared values are 0.286 and 0.602 respectively. These poor fits are again attributed to a small number of experimental data points. In 100%

RR-regression, E decreases from virgin to 1st RG, remains constant from 1st to 3rd RG, and decreases again from 4th to 5th RG. This behavior cannot be observed in 25% and 50% RR samples because 4th and 5th RG samples were not manufactured nor tested.

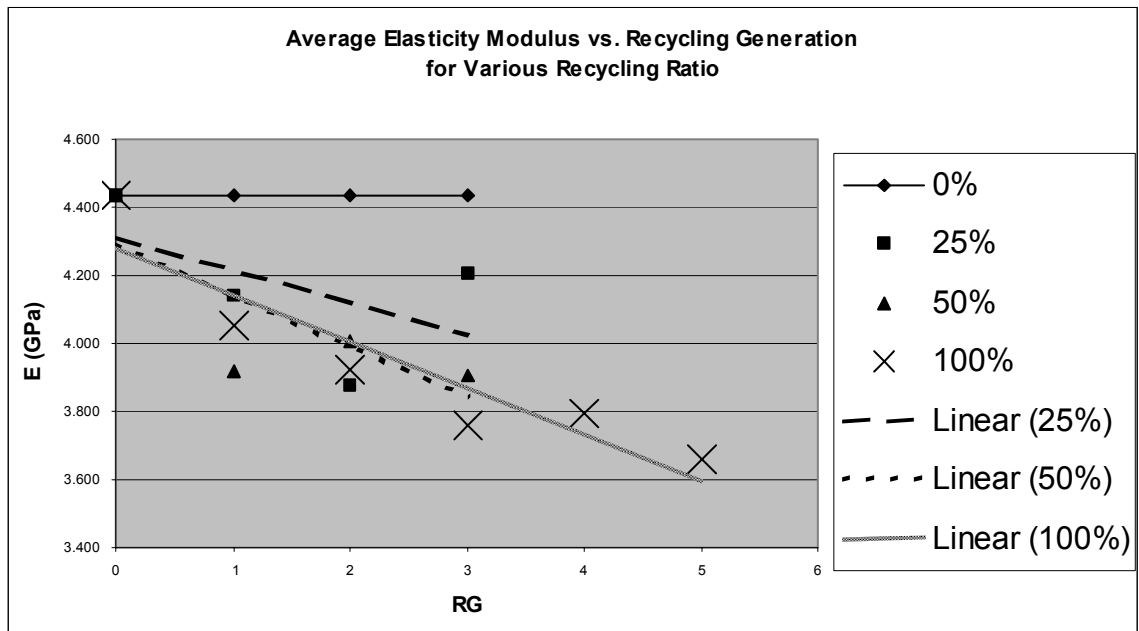


Figure 20: Linear regression for different RR and different generations

Comparison between linear regressions and experimental values can be observed in Table 23. Linear regression shows good fit for 50% and 100% RR, and the maximum difference in regression and experimental values is 5.73%. However, linear regression does not indicate good fit for 50% RR, although the maximum difference in values between regression and experiment was 6.26%. Experimental values for 25%RR remain constant with a distribution of 4.138 ± 0.273 MPa.

Elasticity modulus decreases with RR and RG. The decrease of E has higher rate in 2nd and 3rd RG at same RR. This behavior is the opposite than UTS, but follows traditional theory. Mechanical properties will decrease at higher rate with higher recycled material addition. The fact that UTS has a trend and E has an opposite trend is caused by elongation percent variability. Elasticity modulus is defined by equation 3.2-2, $E = \Delta\sigma / \Delta\varepsilon$. UTS is not affected by Elon. % variability. Otherwise, E is affected because Elongation Percent variability is caused by strain.

Table 23: Experimental and Lineal Fit Comparison for different RR

RG	RR	Experimental	Lineal Fit	Error
0	25%	4.437	4.310	2.88%
1		4.144	4.214	1.69%
2		3.876	4.119	6.26%
3		4.208	4.023	4.40%
0	50%	4.437	4.293	3.25%
1		3.917	4.142	5.73%
2		4.006	3.991	0.39%
3		3.904	3.839	1.65%
0	100%	4.437	4.283	3.47%
1		4.054	4.145	2.25%
2		3.923	4.007	2.13%
3		3.759	3.869	2.92%
4		3.794	3.730	1.67%
5		3.659	3.592	1.82%

Experimental points in Figure 18, shows that E decreases with RR. Linear regression has a good fit for 3rd generation because r-squared values are 0.909. Decreasing behavior can be observed in 1st and 2nd generation too, but linear regression does not fit well with experimental values. In comparing linear regression with experimental values, the maximum difference is only 6.6%. Table 24 compares experimental and linear fit for different RRs.

Table 24: Experimental and Linear Fit Comparison for different RG

RG	RR	Experimental	Linear Fit	Difference
0%	1	4.437	4.293	3.25%
25%		4.144	4.205	1.46%
50%		3.917	4.117	5.08%
100%		4.054	3.940	2.80%
0%	2	4.437	4.229	4.69%
25%		3.876	4.133	6.63%
50%		4.006	4.037	0.76%
100%		3.923	3.844	2.03%
0%	3	4.437	4.375	1.41%
25%		4.208	4.204	0.08%
50%		3.904	4.034	3.35%
100%		3.759	3.694	1.72%

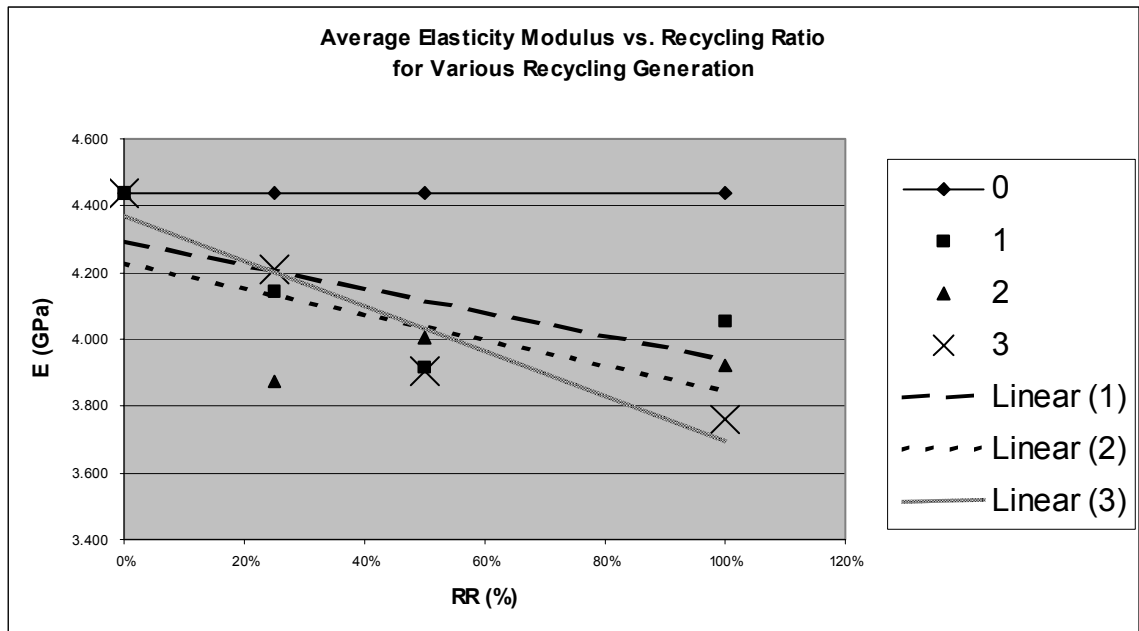


Figure 21: Linear regression for different RG and different ratios.

E distributions for different RRs at same RG follow the same tendency as for 100% RR. The average value decreases with RG during the first generation and remains constant for 2nd and 3rd RG. Distribution for 1st generation and 25% RR is narrower than for virgin material, but 2nd and 3rd generations have the same distribution width as virgin material. This effect can be observed in Figure 21.

Virgin material has a broader distribution than other recycled generations. This means that material has many long than shorter fibers. This causes that the distribution has similar widths until all fibers have similar length. When all fibers have similar lengths, the average value decreases, and distribution is broad. This behavior is shown in Figure 22 and 23.

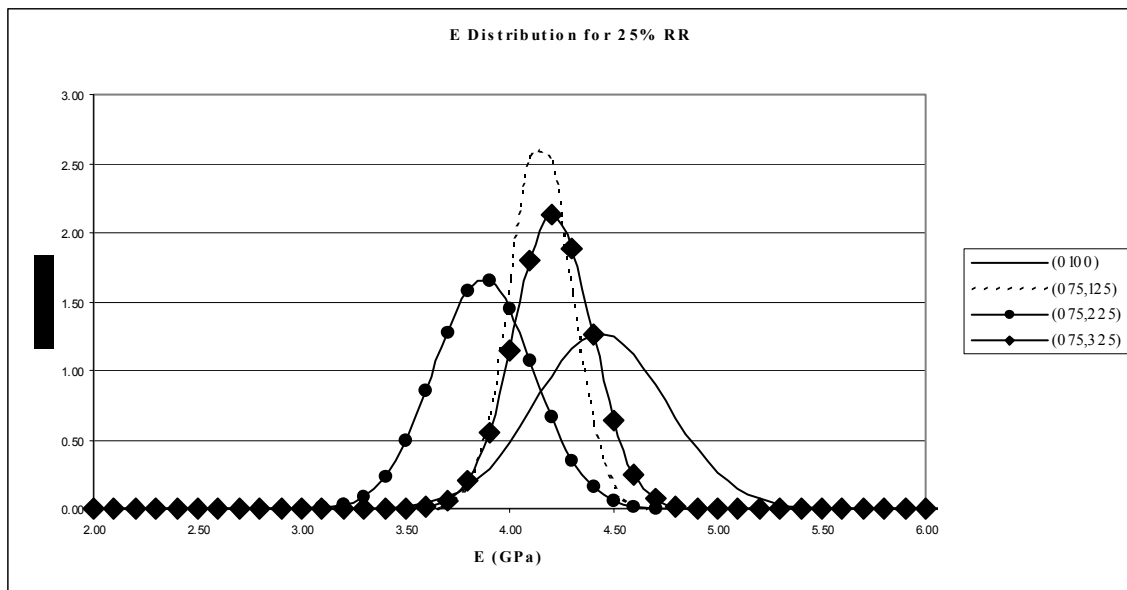


Figure 22: E Distribution for 25%RR

Distribution of values for the 2nd generation shows a similar tendency. For the 1st generation the distribution is narrower than for virgin material, but for the 2nd and 3rd generations the distributions are similar to the virgin samples. Figure 23 shows this behavior. The decrease in average UTS, for RR 25% and 50%, from one RG to the other is not too significant because small percents are not enough to observe big changes.

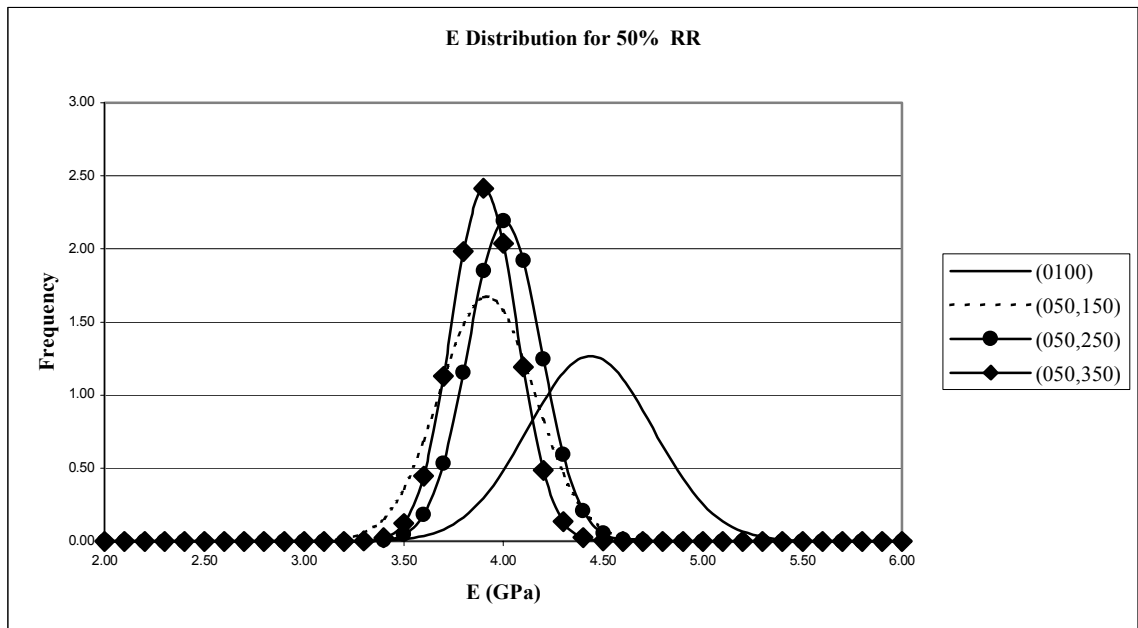


Figure 23: E Distribution for 50%RR

4.1.3.3 Elongation Percent

Elongation percent shows a different trend compared to the mechanical properties described above. The PET material used here contains 15% of glass fibers. Fiber reinforcement loss causes a decrease in mechanical properties like modulus elasticity and ultimate tensile strength, but does not affect percent elongation. Table 25 shows final elongation percent values for all RGs and RRs, and no clear tendency is observed.

Table 25: Average Elon. % values for different RGs and RRs

		Recycling Ratio			
		0%	25%	50%	100%
Recycling Generation	0	1.569%	1.569%	1.569%	1.569%
	1	1.569%	1.694%	1.561%	1.403%
	2	1.569%	1.699%	1.613%	1.599%
	3	1.569%	1.462%	1.768%	1.709%
	4	1.569%	N/A		1.287%
	5	1.569%			1.464%

Elongation percent values have a small range from one RR to the other as can be observed in Table 26. The average range, including all RGs and RRs, is 1.57% ± 0.11%. Elongation percent distribution can be seen in Figures 24 and 25. Each RR and RG values lie inside the virgin material distribution. This behavior proves that elongation percent is not affected by RR or RG variation.

Table 26: Distribution range for Elon. %

RR					
25%		50%		100%	
Average	Range	Average	Range	Average	Range
1.606%	0.140%	1.628%	0.119%	1.505%	0.187%

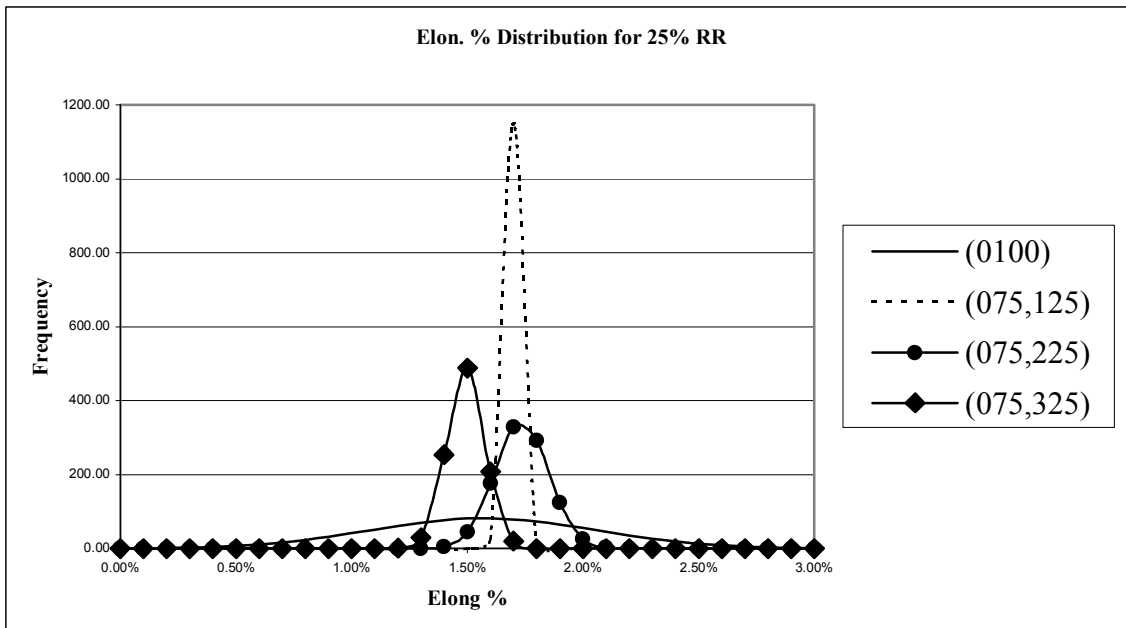


Figure 24: Elon. % Distribution for 25%RR

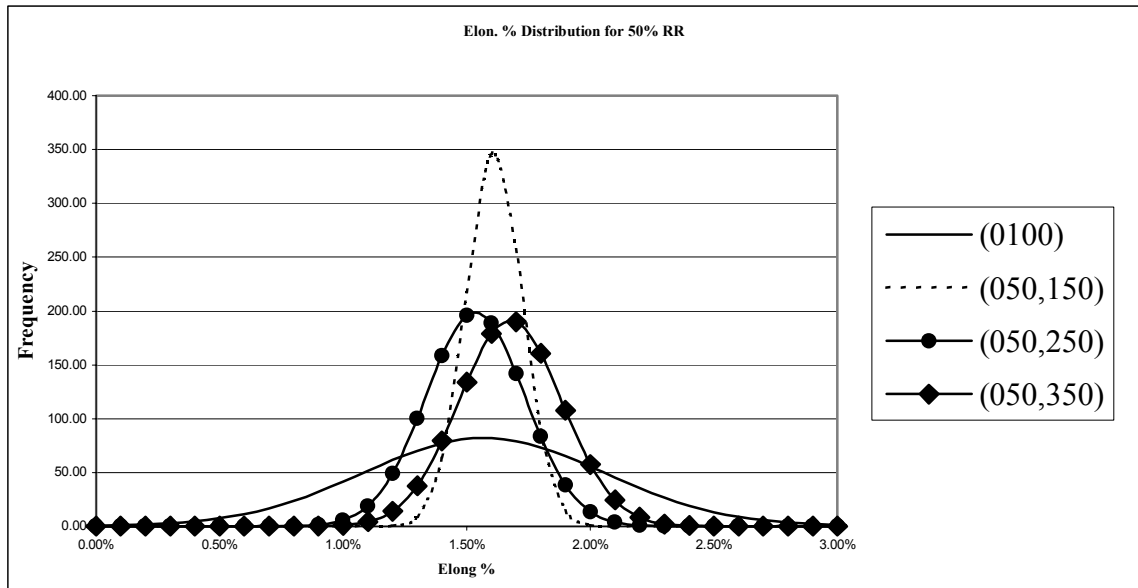


Figure 25: Elong. % Distribution for 50%RR

RG or RR does not affect elongation percent because this property measures the material ability to elongate. This property is dominated by fiber inclusion. The material elongates only if fiber and plastic elongate similarly. Since in this case the fibers elongate less than plastic matrix, elongation is not affected by fiber length, resulting in all the samples having similar values of % elongation to failure.

4.2 Thermal Properties

Thermal properties were measured at least three times to verify values. The thermal properties measured in this study remain constant as a function of recycling generations and recycling ratios. For example, melting temperature range is 259.63 ± 0.58 °C, and glass transition (GT) temperature is 113.60 ± 0.65 °C. Crystallinity percent has a peculiar behavior that will be explained in section 4.2.3.

4.2.1 Glass Transition Temperature

Glass Transition Temperature (GTT) remains constant or has very narrow distribution for different RGs and RRs. For example, GTT range is only 1.41 °C when using 100% RR and different RGs. All experimental values are inside normal t-student distribution and no value was eliminated. Table 27 shows values for varying RG with 100% RR. In this case, average GTT was 113.58 °C with standard deviation of 1.14 °C.

Table 27: Experimental GTT Values and Standard deviation values for RR= 100% and different RG

RG (RR = 100%)	GTT (° C)			Average (° C)	Standard Deviation (° C)
	1	2	3		
(0 ₁₀₀)	112.73	113.02	112.99	112.913	0.159
(0 _{0,1} 100)	114.27	112.75	115.25	114.090	1.260
(0 _{0,2} 100)	113.86	113.92	115.12	114.300	0.711
(0 _{0,3} 100)	111.17	114.87	113.79	113.277	1.903
(0 _{0,4} 100)	111.55	114.44	114.53	113.507	1.695
(0 _{0,5} 100)	113.33	113.95	112.83	113.370	0.561
All				113.576	1.136

Variations in GTT with different RRs are not observed. The average GTT is 113.80 ± 0.62 °C for different RRs. Table 28 shows GTT experimental values.

Table 28: Experimental GTT Values and Standard deviation values for different RG

RG	%RR	GTT (° C)				Average (° C)	Standard Deviation (° C)
		1	2	3	4		
1	25%	113.65	113.80	114.94	114.06	114.11	0.577
1	50%	113.82	113.85	113.73	113.26	113.67	0.275
2	25%	113.24	114.90	113.40	113.71	113.81	0.751
2	50%	113.31	114.33	113.40	113.99	113.76	0.486
3	25%	114.95	114.82	112.98	112.82	113.89	1.149
3	50%	112.90	113.84	113.71	113.69	113.54	0.429
All						113.80	0.623

Graphical representations of GTT distributions are useless because values for all RG and RR are very close to the average value.

RR or RG does not affect thermal properties because chain degradation has not begun. Thermal properties like GTT, defined the energy needed for chain flow. Chain flow is affected by chain length, entanglement, and crosslinkings. Since the material does not have crosslinkings, and assuming that entanglement remains, constant thermal properties are dominated principally by chain length. This means that if GTT does not change, fiber length is similar and degradation has not begun. Besides, even though some chains should be cut during recycling process this is not enough to affect thermal properties, and much less mechanical properties. Fiber length and Crys % dominate mechanical properties, while chain, length dominates thermal properties.

4.2.2 Melting Temperature

Here again, experimental values outside of 95% probability t-distribution were not considered. However, for the thermal properties none of the data points fell outside the 95% probability t-distribution. Melting Temperature (MT) remains constant or has very narrow distribution for different RGs and RRs. For example, MT range is only 0.52 °C when 100% RR is used for different RGs. All experimental values are inside normal t-student distribution. Table 29 shows values of varying RG with RR of 100%. In this case, average GTT was 113.58 °C with a standard deviation of 0.58 °C.

Table 29: Experimental MT Values and Standard deviation values for RR= 100% and different RGs.

RG (RR = 100%)	MT (° C)			Average (° C)	Standard Deviation (° C)
	1	2	3		
(0 ₁₀₀)	259.35	259.26	259.29	259.30	0.045
(0 _{0,1} ₁₀₀)	260.79	259.22	259.23	259.74	0.903
(0 _{0,2} ₁₀₀)	259.96	260.02	260.20	260.06	0.124
(0 _{0,3} ₁₀₀)	260.54	260.20	260.95	260.56	0.375
(0 _{0,4} ₁₀₀)	260.03	260.42	259.17	259.87	0.639
(0 _{0,5} ₁₀₀)	259.63	260.34	259.42	259.79	0.482
All				259.89	0.584

Variations in MT with different RR are not observed. MT average is $259.55^{\circ}\text{C} \pm 0.88^{\circ}\text{C}$ for different RRs. Table 30 shows experimental MT values.

Table 30: Experimental MT Values and Standard deviation values for different RG

RG	%RR	MT (° C)				Average (° C)	Standard Deviation (° C)
		1	2	3	4		
1	25%	259.34	259.17	259.21	260.56	259.14	0.286
1	50%	258.98	259.16	258.88	259.53	258.81	0.449
2	25%	258.83	258.29	258.72	259.38	259.45	0.776
2	50%	259.23	259.03	258.94	260.60	260.09	1.051
3	25%	259.47	259.23	260.09	261.57	260.24	1.247
3	50%	259.31	259.27	261.92	260.44	259.14	0.286
All						259.55	0.883

Graphical representations of MT distributions are meaningless because values for all RG and RR fall in a very narrow band.

In summary, thermal properties are not affected with recycling process. GTT and MT remain constant. This means that degradation is not exhibited because not enough chains were cut.

4.2.3 Crystallinity Percent

Crystallinity percent has different behaviors. When RR = 100% RG varies, crystallinity percent has parabolic fit. Crystallinity percent decreases during first three generations (0 to 2nd RG), stabilizes during the next two generation and increases in 5th RG.

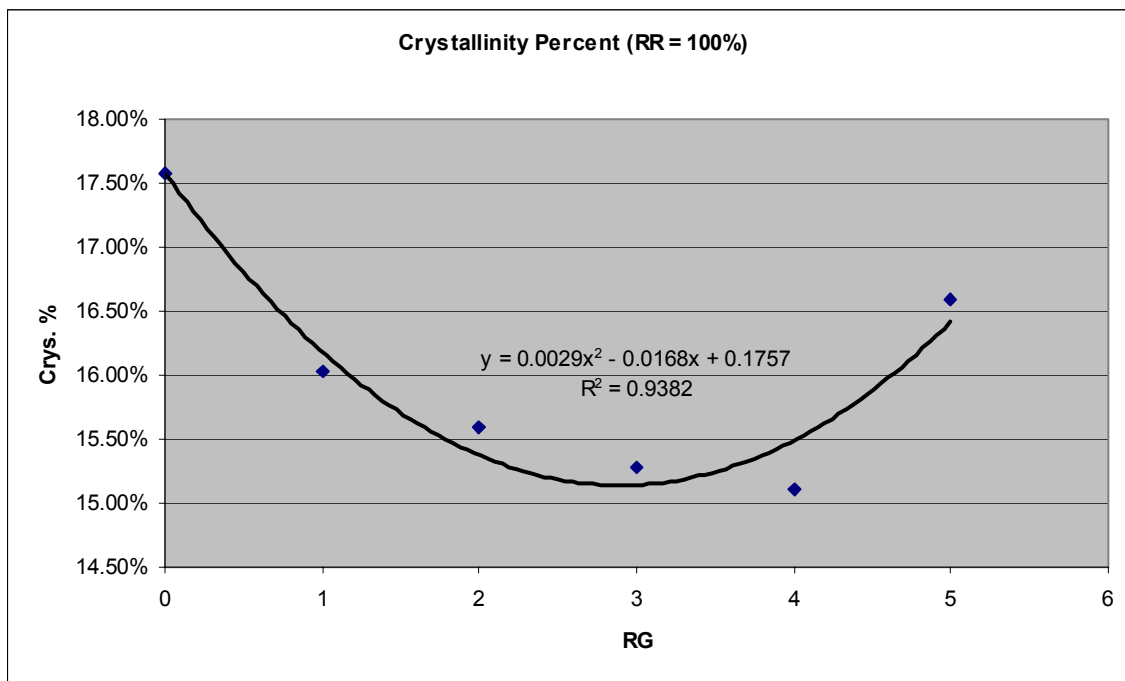


Figure 26: Average and Parabolic Regression for Crys. %

In Figure 26, both parabolic and linear behavior can be observed. The parabolic model has a good fit because the r-squared value is 0.938 and maximum error percent is only 2.54%. Table 31 compares average values with the parabolic regression.

Table 31: Comparison between experimental values and parabolic fit

Sample	Average Crys. %	Crys. % Based on Parabolic Fit	Diff %
(0 ₁₀₀)	17.59%	17.57%	0.09%
(0 _{0,1} ₁₀₀)	16.03%	16.18%	0.93%
(0 _{0,2} ₁₀₀)	15.59%	15.37%	1.40%
(0 _{0,3} ₁₀₀)	15.29%	15.14%	0.96%
(0 _{0,4} ₁₀₀)	15.11%	15.49%	2.54%
(0 _{0,5} ₁₀₀)	16.59%	16.42%	1.01%

None of the data points were eliminated since they did not fall outside the 95%-probability of t-student distribution for different RGs or RRs. Experimental values and their respective standard deviations can be observed in Tables 32 and 33.

Table 32: Experimental Crys. % Values and Standard deviation values for RR= 100% and different RGs

RG (RR = 100%)	Crys. %			Average	Standard Deviation
	1	2	3		
(0 ₁₀₀)	15.80%	18.84%	18.12%	17.59%	1.59%
(0 _{0,1} ₁₀₀)	14.78%	16.34%	16.97%	16.03%	1.13%
(0 _{0,2} ₁₀₀)	15.35%	15.12%	16.30%	15.59%	0.62%
(0 _{0,3} ₁₀₀)	15.20%	13.74%	16.92%	15.29%	1.59%
(0 _{0,4} ₁₀₀)	14.80%	14.15%	16.36%	15.11%	1.13%
(0 _{0,5} ₁₀₀)	16.39%	15.18%	18.19%	16.59%	1.52%
All				16.03%	1.41%

Crystallinity percent has a unique and interesting trend. It decreases during the first RGs, but begins to stabilize in 2nd to 4th generation, same trend that mechanical properties UTS and E, but increases in 5th RG. Crystallinity percent is the chains ability to align or create similar paths inside the plastic material. Align ability increases with chain length. This means that shorter chains align easier than longer ones. The recycling process cuts, decreases length, or causes that chains can align more easily. However this behavior is observed after five complete RG. Crystallinity percent does not increase during previous RG because chains are not short enough to align easily. Crystallinity plateau, 2nd to 4th RG, caused that UTS and E has similar plateau with RG.

Table 33: Experimental Crys. % Values and Standard deviation values for different RG

RG	%RR	Crys. % (° C)				Average (° C)	Standard Deviation (° C)
		1	2	3	4		
1	25%	17.22%	18.97%	14.55%	14.25%	16.25%	2.25%
1	50%	19.63%	16.45%	20.43%	13.85%	17.59%	3.03%
2	25%	18.43%	19.01%	13.29%	14.58%	16.33%	2.82%
2	50%	17.53%	18.70%	20.86%	12.33%	17.36%	3.62%
3	25%	17.12%	18.02%	14.90%	13.10%	15.79%	2.22%
3	50%	17.06%	17.41%	14.35%	14.75%	15.89%	1.56%
All						16.53%	2.46%

Table 34: Summarized Crystallinity Percent Experimental Values with RGs and RRs

		Recycling Ratio			
		0%	25%	50%	100%
Recycling Generation	0	17.585%	17.585%	17.585%	17.585%
	1	17.585%	16.249%	17.589%	16.031%
	2	17.585%	16.326%	17.355%	15.589%
	3	17.585%	15.789%	15.894%	15.287%
	4	17.585%	N/A		15.106%
	5	17.585%			16.588%

The crystallinity percent with different RG does not exhibit a clear behavior, because it decreases or increases randomly. When the combined virgin and recycled material re-align process is stopped, and begins in next RG causing these changes. In third RG, crystallinity percent begins to stabilize, but virgin material inclusion changes final value.

The crystallinity percents for different recycled ratios are also expected to have the same parabolic behavior, but since the 4th and 5th RG samples were not molded to decrease project complexity and cost, this was not observed. Here again, Cryst. Percent decreases during first three generation and stabilizes in the 3rd generation. Consequently, increase in Cryst. Percent is not observed because of lack of data points.

The distribution of these values can be observed in Figures 27 and 28. Width distribution is very similar from 0 to 3rd RG, but the average value decreases in some generations. This behavior is observed for RR = 25% and 50%.

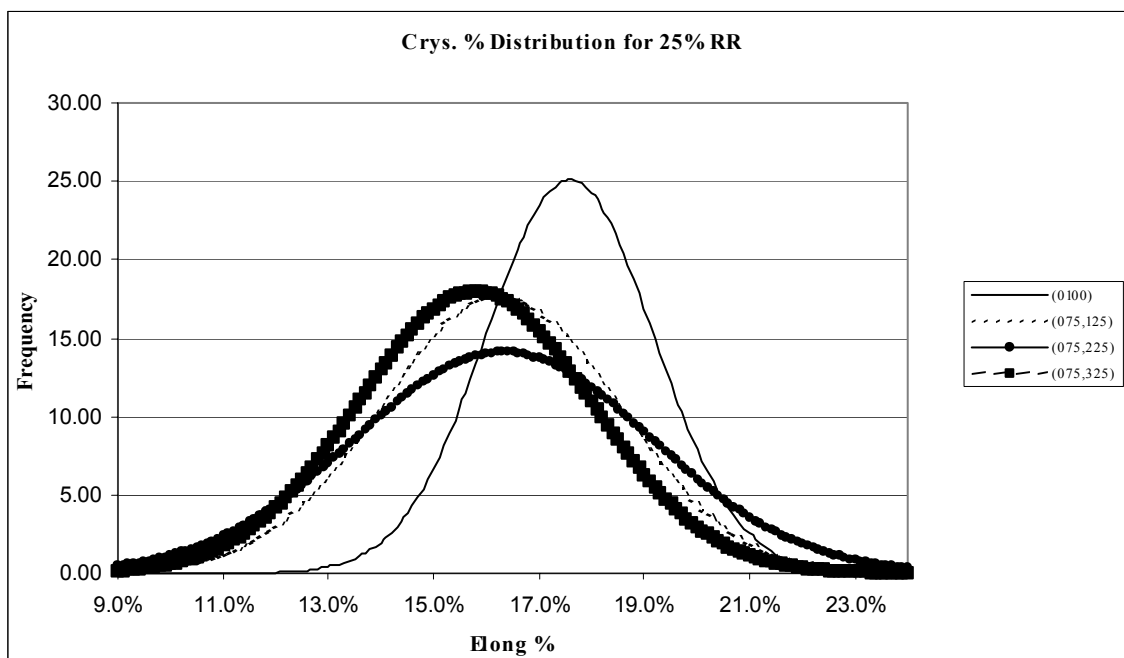


Figure 27: Crys. % Distribution for 25%RR

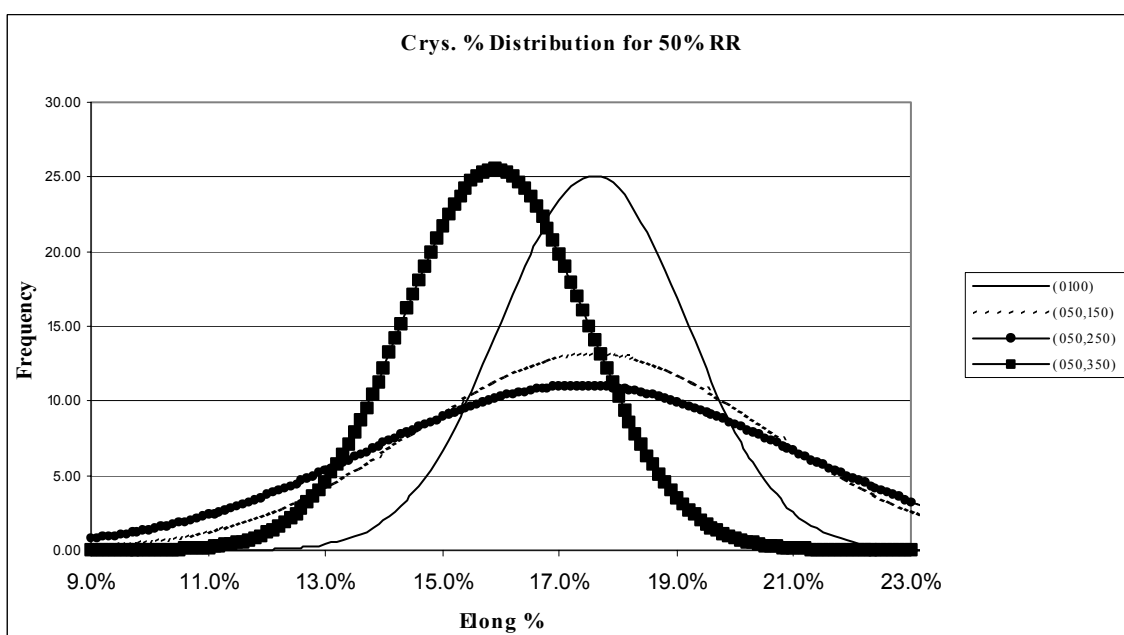


Figure 28: Crys. % Distribution for 50%RR

Crystallinity percent distributions have similar widths with different RR. These show that re-aligning process is not observed before 4th RG at any RR. For this reason, crystallinity percent average values and distribution width is not affected.

4.3 Additional Observations

In summary, recycled ratio and recycled generation, especially, could result in a decrease in the mechanical properties of the material. 3-D models could not be generated because more data points are needed. Typical behavior for UTS, E, and Crys. % shows:

- During 0 (virgin) to 2nd or 3rd RG, there is a decrease in properties
- From 2nd to 4th RG, no further property loss is observed.
- In 5th RG material, mechanical properties diminish again, but Crys. % increases.

Thermal properties like GTT and MT do not change and distributions are extremely narrow, indicating tremendous consistency in the data because thermal degradation, polymeric chains shortage is not observed.

Chapter 5: Conclusions and Recommendations

The research objectives were to verify if material properties change with recycling process, identify additional factors that change properties, analyze and determine clear property tendencies, generate calibration curves; verify the number of recycled generations that can be permitted before material exhibits degradation, create an alternative process to resin vendor rules of thumb, change current recycled material perspective as low performance materials, and increase recycled materials usage. Some objectives were achieved and analyzed, but future investigations and industry support are needed to reach the other goals. In summary, material properties do change with recycling, but using rules of thumb is not a good method to predict material behavior.

5.1 Mechanical Properties

It is obvious from the experimental data that the mechanical properties are affected as a result of recycling. Principally, mechanical properties decrease with RR and RGs. From the last chapter, it was discussed that mechanical properties are affected by recycling because fiber length decreases and crystallinity percent changes. Chain length does not affect mechanical properties because degradation is exhibited after many recycling generations.

In theory, mechanical properties increase with any fiber inclusion resulting in better mechanical properties compared to monolithic PET [14, 16]. Filler inclusion reinforces material because stress is distributed between matrix and fiber material [14, 16]. However, fiber length is critical for effective reinforcement of a material. In this research, after 3rd RG the fiber length is too short and the material behaves like a non-reinforced material. Crystallinity percent increase improves mechanical properties because this increases the bonding energy between chains [14]. This increase in mechanical properties works in contrast to the decrease in fiber length. Following described behavior; the change in mechanical properties can be described by:

$$\Delta MP = \Delta FL + \Delta CL + \Delta C\% + \Delta RE + \Delta EN \quad (5.1-1)$$

where ΔMP is change in mechanical properties, ΔFL = change in fiber length, ΔCL is change in average polymeric chain length, $\Delta C\%$ is the change in crystallinity percent, ΔRE is the change or addition of re-constituents, and ΔEN = change in chain entanglement.

In this research, $\Delta RE = \Delta EN = \Delta CL = 0$. $\Delta RE = 0$ because re-constituents substances were not added to improve mechanical properties. $\Delta EN = 0$ was assumed since it is difficult to measure and special equipment is needed. $\Delta CL = 0$, because GTT and MT do not change during thermal property determination. This also means that chain length does not change [14]. For this reason only two factors, crystallinity percent and glass fiber length, which act one against other contribute to change in the mechanical properties.

In conclusion,

1. Glass fiber length decrease during the recycling process causes loss in mechanical properties such as UTS and E. However, some of this is recovered by increase in crystallinity percent. While fiber length decreases during each recycling step, crystallinity percent remains constant and increase after 5th RG.
2. Elongation percent is not affected by crystallinity percent or fiber shortage and follows a t-student distribution.
3. Mechanical properties decrease only 6.0% maximum per RG using RR = 100%. This is not adequate enough to affect many plastic designs, because the above decrease will be covered by the designer's safety factor.
4. Mechanical properties losses should not be considered in the decision to add recycled plastics to new products because:
 - a. Loss amounts are not significant.
 - b. Manufactures could improve mechanical properties by molding at a lower temperature (increase crystallinity

percent), add re-constituents, or use virgin-recycled plastics mixtures.

5. Recycled plastics are not necessarily low performance materials. They should be described as not studied materials, since the lack of research.
6. Rules of thumb, 25% or less of RR, is not a good estimate because more material can be added without having a significant impact on the mechanical properties.
7. Using recycled material tends to decrease mechanical properties during 1st RG, remains constant during 2nd to 4th RG and decreases again in 5th RG. Besides, a good estimate for this trend is a linear regression.
8. 3-D calibration curves have not be generated because experimental points are lacking.

5.2 Thermal Properties

Secondly, plastic compounds contain polymer chains. The recycling process breaks some of the polymer chains, but this is usually not enough to cause material degradation. For this reason, thermal properties in plastics are not affected by thermal history until almost all polymer chains are cut. The shortening of the polymer chains as a result of breakage during the recycling process is not as dominant as the fiber breakage and hence probably makes only a minor contribution to the overall decrease in strength and rigidity.

For this reason, it can be concluded that:

1. Chain length is not affected by recycling process during the first 5th RG. Thermal degradation is not exhibit in research range, 0% to 100% of RR and five recycled generations.
2. Crystallinity percent is a predominant and very important value in PET. Crys. % could improve or decrease material properties very

easily. Good manufacturer practices should be including improving material properties.

3. Besides, Mechanical and Thermal properties are related to chain length. Chain length is not the unique factor that affects plastics materials.

5.3 Recommendations

Recycled materials should be used in new products because this is a win-win situation. Recycled materials generally are cheaper than virgin materials and plastics producers can reduce environmental impacts.

Results research errors could be minimized if some recommendations are followed:

1. Perform all tension tests in same tension machine.
2. Select a broad scope and have additional founding to get better results and trends in bigger range.
3. Perform test with unreinforced plastic to verify mechanical properties losses and validate degradation model.
4. Measure additional properties like impact toughness, viscosity, torsion stress, flexional stress, and density.

In order to complete recycled material research, some steps to increase academy and industry knowledge in plastics materials are suggested. These steps are:

1. Perform additional research to continue this work. New researchers should quantify additives losses, polymeric chains and fibers shortage, and measure chains entanglement.
2. Run same research with different materials and common use plastics like: HDPE, LDPE, PVC, PS, PP, PC, ABS, HIPS, etc.

3. Environmental regulatory agencies or measurement standard agencies should create qualification and measurement standards to add recycled materials to new products.
4. Worldwide, governments should approve environmental regulations that support recycled plastics collection and inclusion in new products.
5. Use recycled materials in new products. Other manufacturers should change their perspective to design products which are environmentally friendly including post consumer plastics in new products.

Chapter 6: References

1. Solid Waste Authority Research. *Puerto Rico Solid Waste Characterization*. 1993.
2. Municipal Solid Waste in the United States 1999 Facts and Figures". www.epa.gov/seahome/housewaste/src/plastic.htm (May 2003).
3. Buchanan, R., PhD. U.S. Food and Drug Administration, Center for Food and Applied Nutrition. *FDA/CFSAN Priority Research Needs*. August 2000.
4. U.S Department of Health and Human Services, Food and Drug Administration, *Center for Drug Evaluation and Research, Center for Biologics Evaluation and Research*. May 1999. p 17
5. Eulálio, A.C., Capiati, N.J., and Barbosa, S. 2001. Plapiqui (UNS Concinet) c.c. 717. *Municipal Plastic Waste: Alternatives for recycling with profit*. Annual Technical Conference (ANTEC). May, 2000. <http://www.sperecycling.org/PDF%20Files/0805.PDF>
6. Kukaleva, N., Simon, G., and Kosior, E.2001. *The effect of blending on the viscosity reduction of recycled milk Bottle Grade HDPE*. Annual Technical Conference (ANTEC). May, 2001. <http://www.sperecycling.org / PDF%20Files / 0675.PDF>
7. Lynch, J.K., Nosker, T.J., Renfree, R.W., Krishnaswany, P., Francini, R. 2001. *Weathering effects on mechanical properties of recycled HDPE based plastic lumber*. Annual Technical Conference (ANTEC). May, 2001 <http://www.sperecycling.org /PDF%20Files /0951.PDF>

8. Miller, P., Kosior, E., Masood, S., and Iovenitti, P. 2001. *Linearity and non-linearity of mechanical properties in blends of virgin and recycled HDPE's*. 8th Annual Global Plastics Environmental Conference. Detroit, United States. 2002. <http://www.sperecycling.org/PDF%20Files/0646.PDF>
9. Trahan, J.S., Hayden, K., and Engelmann, P. 2001. *Impact of fines on reinforced thermoplastic regrind*. 8th Annual Global Plastics Environmental Conference. Detroit, United States. 2002. www.sperecycling.org/PDF%20Files/0676.PDF
10. Powell, J. PET By Numbers. *Plastic Recycling Updates Newsletter*. July 2003 to July 2004. p 1.
11. Mackey, J, & Celorie, J. *Recycling Inkjet Cartridge and Closing the Loop with Recycled Plastic*. 8th Annual Global Plastics Environmental Conference – Proceedings Book. Detroit, United States, 2002. p 41
12. GE Plastics. *PET Datasheet* (Limited Use). 2002.
13. Liang, R., and Gupta, R.K. 2001. *Rheological and mechanical properties of recycled polycarbonate*. XIIIth International Congress on Rheology, Cambridge, UK, August 20-25, 2000. <http://www.sperecycling.org/PDF%20Files/0476.PDF>
14. Strong, A.B. Micro Structures in Polymers. *Polymeric Composite Materials and Processes. Environmental Aspects of Plastics*. In *Plastic Materials and Processing*. Prentice Hall, New Jersey, USA 1996. pp 69-82, 481-492, 606, 609-616.
15. Sperling, L.H. Introduction to Polymer Science. Molecular Weights and Sizes. The Crystalline State. In *Introduction to Physical Polymer Science*. John Wiley and Sons, Inc, Pennsylvania, United States 1992. pp 14, 108-110, 269.

16. Chawla K.K., Composite Materials, Springer-Verlag, New York, 1987.
17. Polyethylene Terephthalate (PET), Unreinforced and Glass/Mineral Reinforced. <http://www.matweb.com> (accessed November 2002).
18. Stevens, M.P. Chemical Structure and Polymer Morphology. In *Polymer Chemistry An Introduction*. Oxford University Press, New York, United States, 1999. p 80.
19. Standard Test Method for Tensile Properties of Plastics. *American Standards of Testing Materials D638*. 1992. pp 1-25
20. *Basic Theory and Applications in Differential Scanning Calorimetry*, TA Instruments, Inc.

Appendix 1

1.1 Mechanical Properties Statistical Data

1.1.1 Ultimate Tensile Strength

Table 35: UTS Average and Standard Deviation RR = 100%

RG	Sample #					Average	Standard Deviation
	1	2	3	4	5		
0	63.937	70.432	45.874	59.898	57.291	59.486	9.0816
1	41.507	68.557	55.066	55.721	54.106	54.991	9.5811
2	54.957	64.143	52.805	58.804	48.226	55.787	6.0349
3	54.390	55.996	55.108	54.450	55.648	55.119	0.7119
4	35.408	46.168	47.131	50.558	46.364	45.126	5.7137
5	40.648	49.056	53.241	43.265	40.140	45.270	5.6915

*Values outside 95% probability of t-student distribution

Table 36: UTS Range, Minimum, and Maximum Values in t-student distribution with RG = 100%

RG	Range	Min	Max
0	11.250	48.236	70.736
1	11.869	43.122	66.860
2	7.476	48.311	63.263
3	0.882	54.237	56.001
4	7.078	38.048	52.204
5	7.051	38.219	52.321

Table 37: UTS Average and Standard Deviation at Various RRs and RGs

RG	RR	Sample #					Average	Standard Deviation
		1	2	3	4	5		
1	25%	61.125	62.565	62.441	62.972	61.954	62.211	0.7077
1	50%	57.340	51.086*	59.350	58.489	0.000*	56.566	3.7453
2	25%	63.970	54.862*	66.752	58.166	62.384	61.227	4.7244
2	50%	56.443	56.565	62.013	49.768*	58.779	56.713	4.4914
3	25%	61.441*	57.902	57.690	54.401	56.186	57.524	2.6009
3	50%	63.707	52.841*	63.441	64.607	58.92	60.703	4.9180

*Values outside 95% probability of t-student distribution

Table 38: UTS Range, Minimum, and Maximum Values in t-student distribution at Various RGs and RRs

RG	RR	Range	Min	Max
1	25%	11.250	48.236	70.736
1	50%	11.869	43.122	66.860
2	25%	7.476	48.311	63.263
2	50%	0.882	54.237	56.001
3	25%	7.078	38.048	52.204
3	50%	7.051	38.219	52.321

1.1.2 Elasticity Modulus

Table 39: E Average and Standard Deviation RR = 100%

RG	Sample #					Average	Standard Deviation
	1	2	3	4	5		
0	3.506*	4.288	4.716	4.065	4.679	4.251	0.4976
1	4.122	0.000*	4.114	3.675*	3.925	3.959	1.7798
2	3.928	4.000	3.732*	3.800	3.965*	3.885	0.1143
3	3.828	3.773	3.732	3.703	3.555	3.718	0.1025
4	3.524*	3.894	3.926	3.674	3.681	3.740	0.1679
5	3.458	3.804	3.758	3.429	3.844	3.659	0.1989

*Values outside 95% probability of t-student distribution

Table 40: E Range, Minimum, and Maximum Values in t-student distribution with RG = 100%

RG	Range	Min	Max
0	0.616	3.635	4.868
1	2.205	1.754	6.164
2	0.142	3.743	4.027
3	0.127	3.591	3.845
4	0.208	3.532	3.948
5	0.246	3.412	3.905

Table 41: E Average and Standard Deviation at Various RRs and RGs

RG	RR	Sample #					Average	Standard Deviation
		1	2	3	4	5		
1	25%	4.230	4.057	4.203	4.277	3.953	4.144	0.1348
1	50%	4.078	3.364*	3.672	4.003	0.000*	3.779	0.3281
2	25%	4.093	3.591	3.831	3.375*	3.987	3.776	0.2930
2	50%	3.810	4.184	3.959	4.170	3.908	4.006	0.1652
3	25%	3.966	4.345	4.213	3.807*	4.308	4.128	0.2322
3	50%	3.141*	4.524	4.041*	3.927	3.743	3.875	0.5020

*Values outside 95% probability of t-student distribution

Table 42: E Range, Minimum, and Maximum Values in t-student distribution at Various RGs and RRs

RG	RR	Range	Min	Max
1	25%	0.167	3.977	4.311
1	50%	0.406	3.373	4.186
2	25%	0.363	3.413	4.139
2	50%	0.205	3.801	4.211
3	25%	0.288	3.840	4.416
3	50%	0.622	3.253	4.497

1.1.3 Elongation Percent

Table 43: Elon. % Average and Standard Deviation RR = 100%

RG	Sample #					Average	Standard Deviation
	1	2	3	4	5		
0	1.823%	2.274%*	0.972%*	1.470%	1.415%	1.591%	0.487%
1	1.105%	0.000%*	1.537%	1.668%	1.303%	1.403%	0.664%
2	1.796%	2.021%	1.452%	1.125%	3.040%*	1.887%	0.729%
3	1.667%	3.599%*	1.666%	1.639%	1.864%	2.087%	0.850%
4	1.082%*	1.330%	1.280%	1.482%*	1.251%	1.285%	0.144%
5	1.290%	1.492%	1.594%	1.478%	1.044%*	1.380%	0.217%

*Values outside 95% probability of t-student distribution

Table 44: Elon. % Range, Minimum, and Maximum Values in t-student distribution with RG = 100%

RG	Range	Min	Max
0	0.603%	0.987%	2.194%
1	0.822%	0.581%	2.225%
2	0.903%	0.984%	2.790%
3	1.053%	1.034%	3.140%
4	0.179%	1.106%	1.464%
5	0.269%	1.110%	1.649%

Table 45: Elon. % Average and Standard Deviation at Various RRs and RGs

RG	RR	Sample #					Average	Standard Deviation
		1	2	3	4	5		
1	25%	1.664	1.729	1.680	1.664	1.732	1.694	0.034
1	50%	1.483	1.603	1.762*	1.596	0.000*	1.611	0.115
2	25%	1.683	1.592	1.827	1.879*	1.692	1.735	0.116
2	50%	1.607	1.458	1.723	1.223*	1.665	1.535	0.200
3	25%	1.618*	1.512	1.422	1.496	1.419	1.493	0.081
3	50%	1.776	1.310*	1.766	1.820	1.710	1.676	0.209

*Values outside 95% probability of t-student distribution

Table 46: Elon. % Range, Minimum, and Maximum Values in t-student distribution at Various RGs and RRs

RG	RR	Range	Min	Max
1	25%	0.042	1.651	1.736
1	50%	0.142	1.469	1.753
2	25%	0.144	1.590	1.879
2	50%	0.248	1.287	1.783
3	25%	0.101	1.393	1.594
3	50%	0.258	1.418	1.935

1.2 Thermal Properties Statistical Data

1.2.1 Glass Transition Temperature

Table 47: GTT Average and Standard Deviation RR = 100%

RG	Sample #			Average	Standard Deviation
	1	2	3		
0	112.73	113.02	112.99	112.913	0.1595
1	114.27	112.75	115.25	114.090	1.2597
2	113.86	113.92	115.12	114.300	0.7108
3	111.17	114.87	113.79	113.277	1.9027
4	111.55	114.44	114.53	113.507	1.6951
5	113.33	113.95	112.83	113.370	0.5611

Table 48: GTT Range, Minimum, and Maximum Values in t-student distribution with RG = 100%

RG	Range	Min	Max
0	0.198	112.716	113.111
1	1.560	112.530	115.650
2	0.880	113.420	115.180
3	2.357	110.920	115.634
4	2.100	111.407	115.607
5	0.695	112.675	114.065

Table 49: GTT Average and Standard Deviation at Various RRs and RGs

RG	RR	Sample #				Average	Standard Deviation
		1	2	3	4		
1	25%	113.65	113.80	114.94	114.06	114.11	0.577
1	50%	113.82	113.85	113.73	113.26	113.67	0.275
2	25%	113.24	114.90	113.40	113.71	113.81	0.751
2	50%	113.31	114.33	113.40	113.99	113.76	0.486
3	25%	114.95	114.82	112.98	112.82	113.89	1.149
3	50%	112.90	113.84	113.71	113.69	113.54	0.429

Table 50: GTT Range, Minimum, and Maximum Values in t-student distribution at Various RGs and RRs

RG	RR	Range	Min	Max
1	25%	1.192	112.921	115.304
1	50%	0.567	113.098	114.232
2	25%	1.550	112.262	115.363
2	50%	1.004	112.753	114.762
3	25%	2.373	111.520	116.265
3	50%	0.885	112.650	114.420

1.2.2 Melting Temperature

Table 51: MT Average and Standard Deviation RR = 100%

RG	Sample #			Average	Standard Deviation
	1	2	3		
0	259.35	259.26	259.29	259.300	0.046
1	260.79	259.22	259.23	259.747	0.904
2	259.96	260.02	260.20	260.060	0.125
3	260.54	260.20	260.95	260.563	0.376
4	260.03	260.42	259.17	259.873	0.640
5	259.63	260.34	259.42	259.797	0.482

Table 52: MT Range, Minimum, and Maximum Values in t-student distribution with RG = 100%

RG	Range	Min	Max
0	0.057	259.243	259.357
1	1.119	258.627	260.866
2	0.155	259.905	260.215
3	0.465	260.098	261.029
4	0.792	259.081	260.666
5	0.597	259.199	260.394

Table 53: MT Average and Standard Deviation at Various RRs and RGs

RG	RR	Sample #				Average	Standard Deviation
		1	2	3	4		
1	25%	259.34	259.17	259.21	260.56	259.57	0.664
1	50%	258.98	259.16	258.88	259.53	259.14	0.286
2	25%	258.83	258.29	258.72	259.38	258.81	0.449
2	50%	259.23	259.03	258.94	260.60	259.45	0.776
3	25%	259.47	259.23	260.09	261.57	260.09	1.051
3	50%	259.31	259.27	261.92	260.44	260.24	1.247

Table 54: MT Range, Minimum, and Maximum Values in t-student distribution at Various RGs and RRs

RG	RR	Range	Min	Max
1	25%	1.371	258.199	260.941
1	50%	0.591	258.547	259.728
2	25%	0.926	257.879	259.731
2	50%	1.603	257.847	261.053
3	25%	2.170	257.920	262.260
3	50%	2.576	257.659	262.811

1.2.3 Crystallinity Percent

Table 55: Crys. % Average and Standard Deviation RR = 100%

RG	Sample #			Average	Standard Deviation
	1	2	3		
0	15.796%	18.837%	18.123%	17.585%	1.590%
1	14.782%	16.338%	16.974%	16.031%	1.127%
2	15.346%	15.125%	16.296%	15.589%	0.622%
3	15.203%	13.740%	16.916%	15.287%	1.590%
4	14.804%	14.154%	16.360%	15.106%	1.133%
5	16.388%	15.182%	18.194%	16.588%	1.516%

Table 56: Crys. % Range, Minimum, and Maximum Values in t-student distribution with RG = 100%

RG	Range	Min	Max
0	1.970%	15.615%	19.555%
1	1.397%	14.635%	17.428%
2	0.770%	14.818%	16.359%
3	1.969%	13.317%	17.256%
4	1.404%	13.702%	16.510%
5	1.878%	14.710%	18.466%

Table 57: GTT Average and Standard Deviation at Various RRs and RGs

RG	RR	Sample #				Average	Standard Deviation
		1	2	3	4		
1	25%	17.223%	18.965%	14.554%	14.254%	16.249%	2.249%
1	50%	19.629%	16.453%	20.428%	13.847%	17.589%	3.028%
2	25%	18.430%	19.008%	13.291%	14.575%	16.326%	2.822%
2	50%	17.530%	18.701%	20.857%	12.334%	17.355%	3.620%
3	25%	17.123%	18.023%	14.904%	13.105%	15.789%	2.218%
3	50%	17.059%	17.409%	14.354%	14.754%	15.894%	1.563%

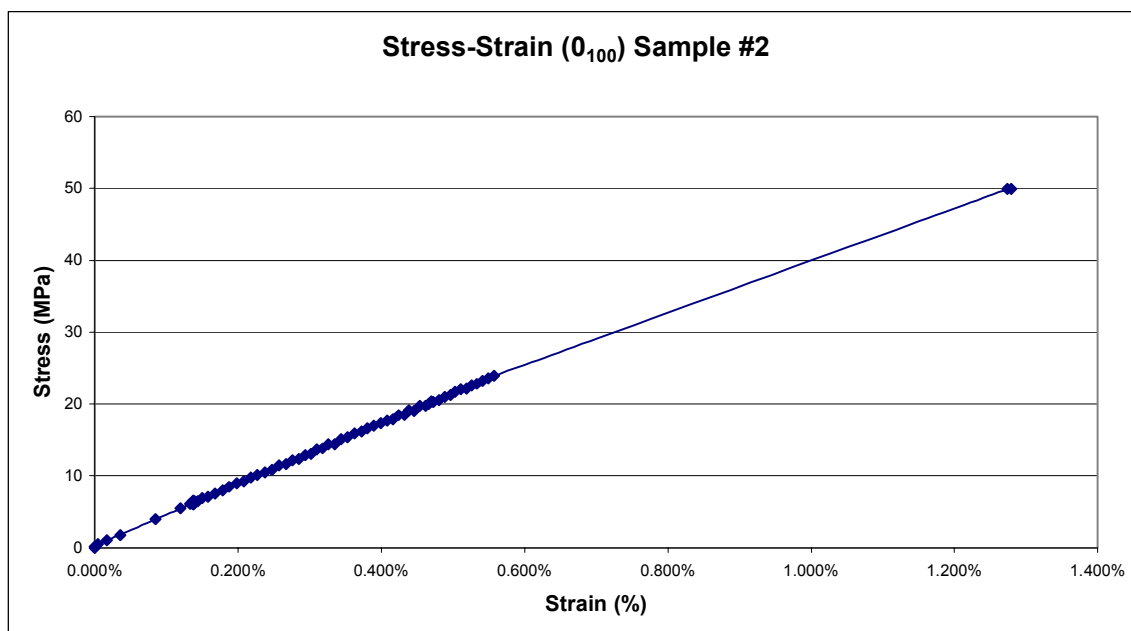
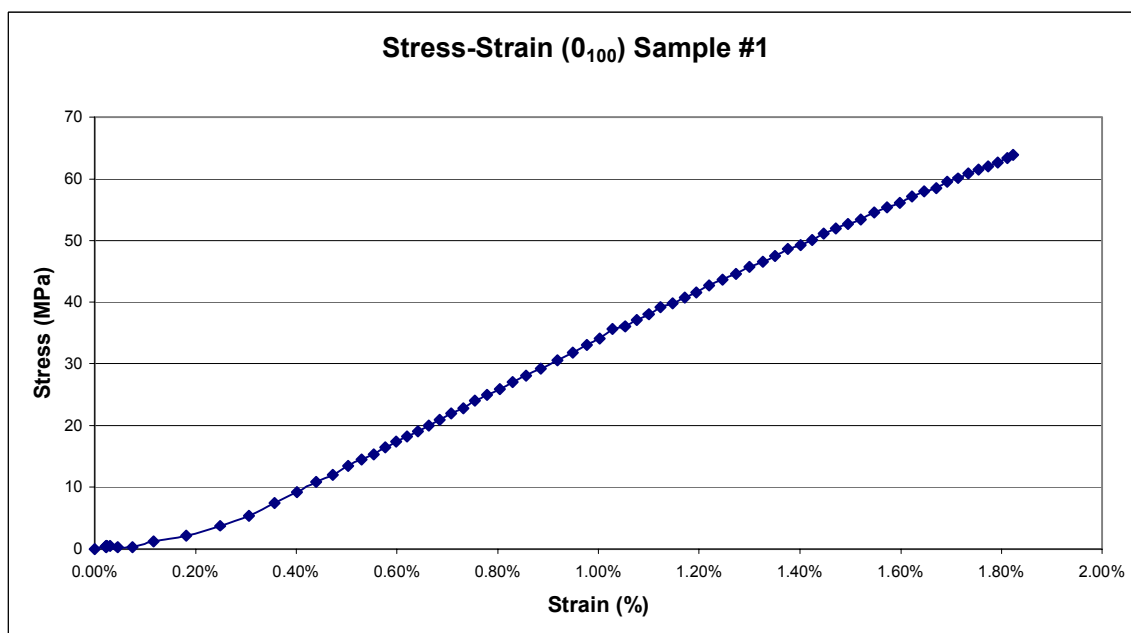
Table 58: GTT Range, Minimum, and Maximum Values in t-student distribution at Various RGs and RRs

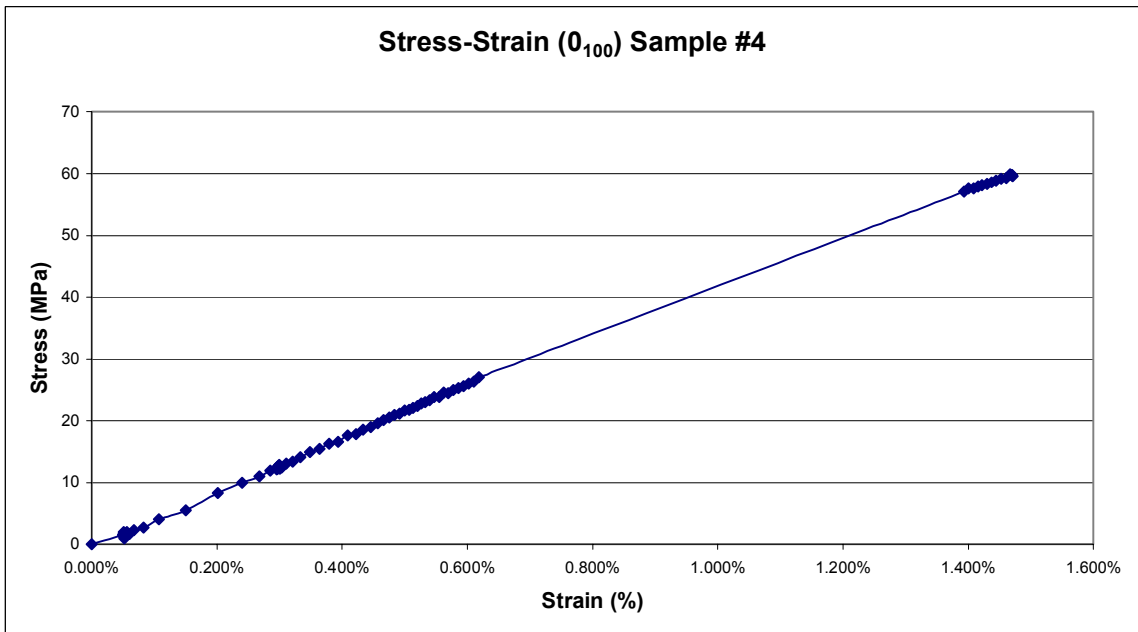
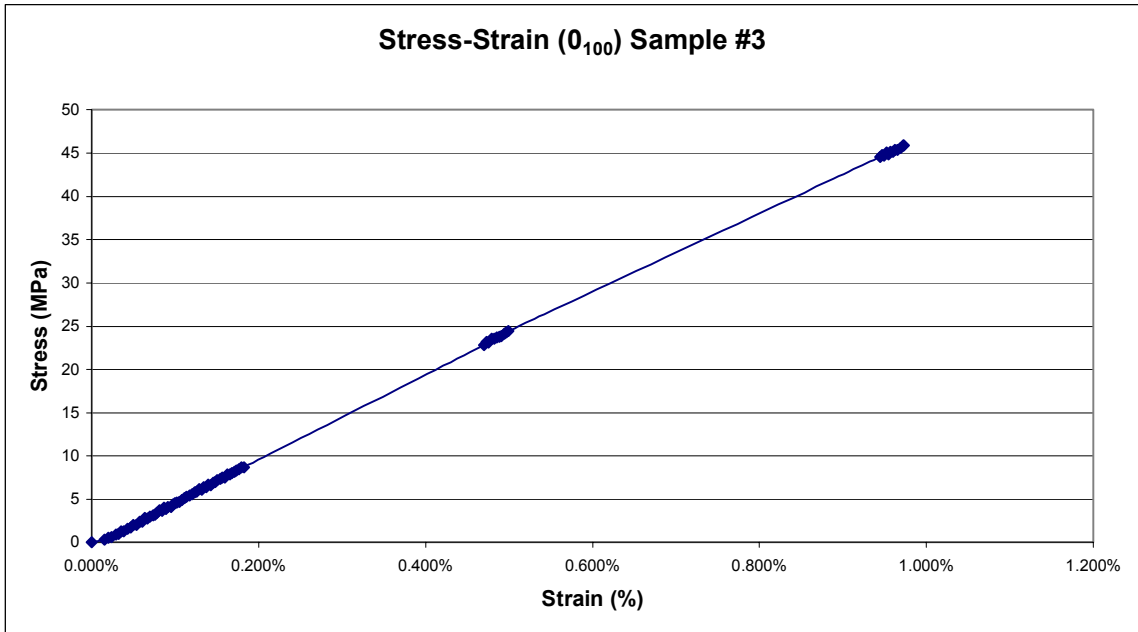
RG	RR	Range	Min	Max
1	25%	4.644%	11.605%	20.894%
1	50%	6.253%	11.336%	23.842%
2	25%	5.827%	10.498%	22.153%
2	50%	7.474%	9.881%	24.830%
3	25%	4.580%	11.209%	20.368%
3	50%	3.226%	12.668%	19.120%

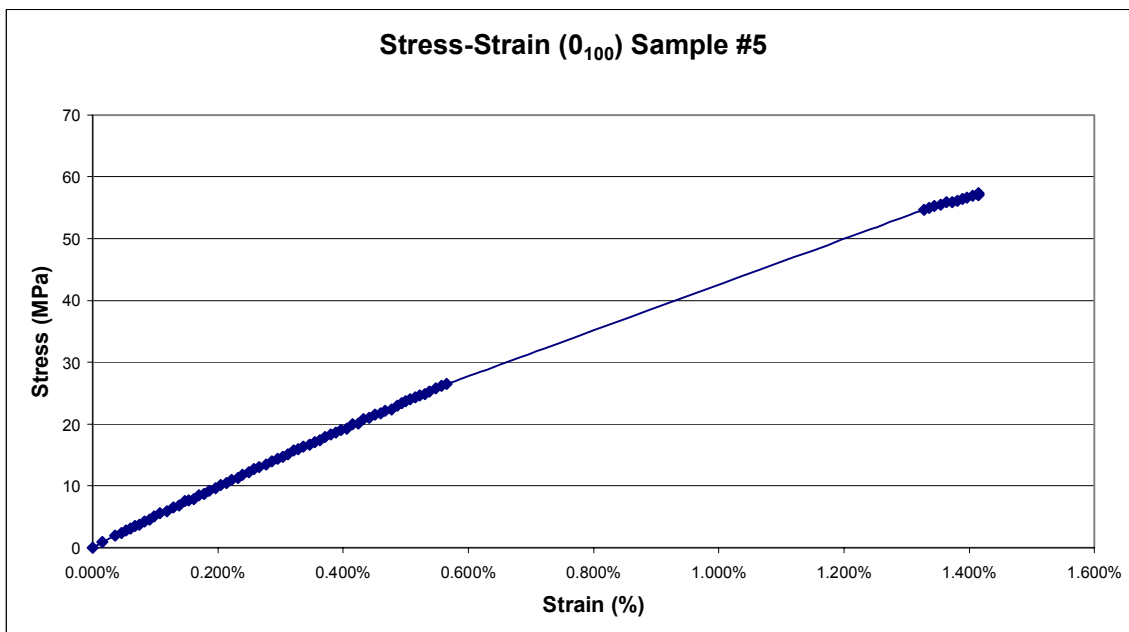
Appendix 2: Stress-Strain Diagrams

2.1 Different RG and RR= 100%

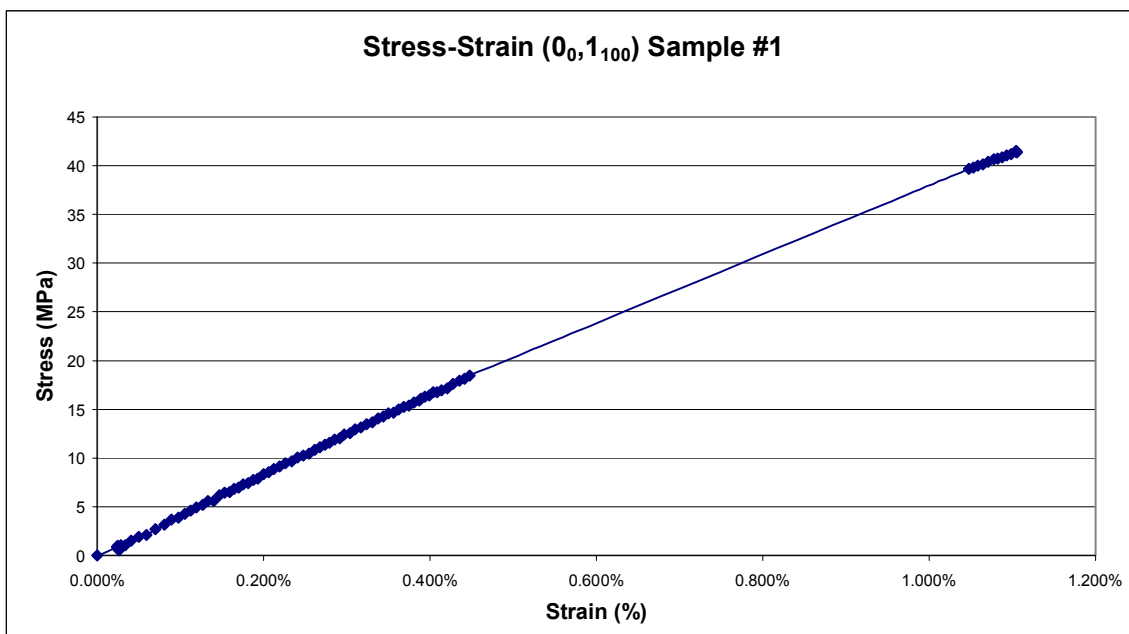
2.1.1 Virgin Curves

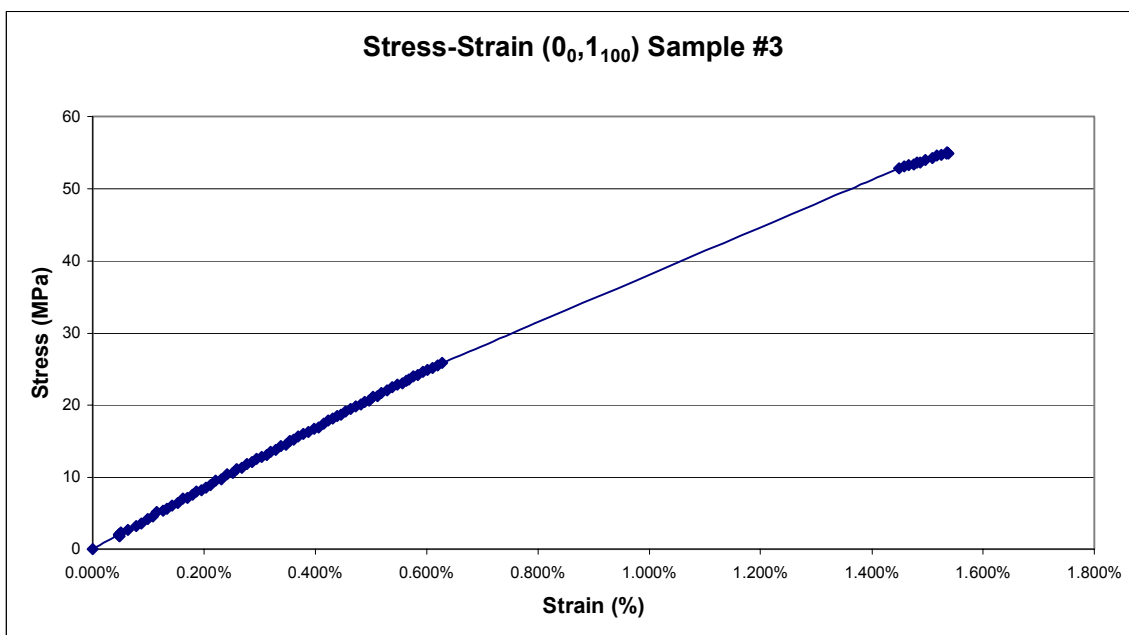
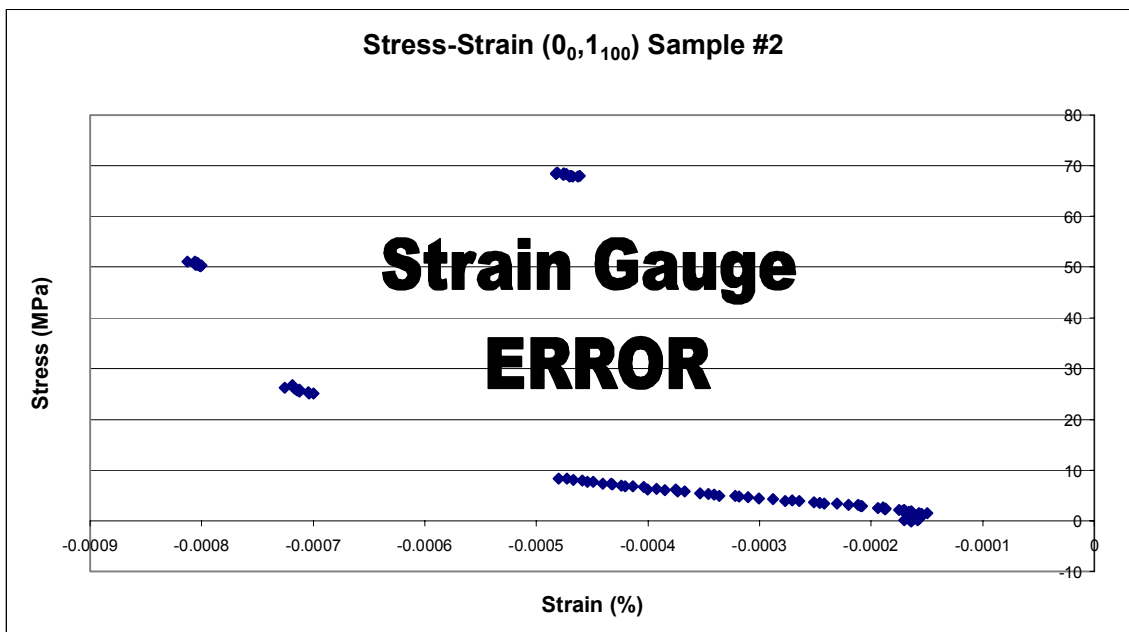


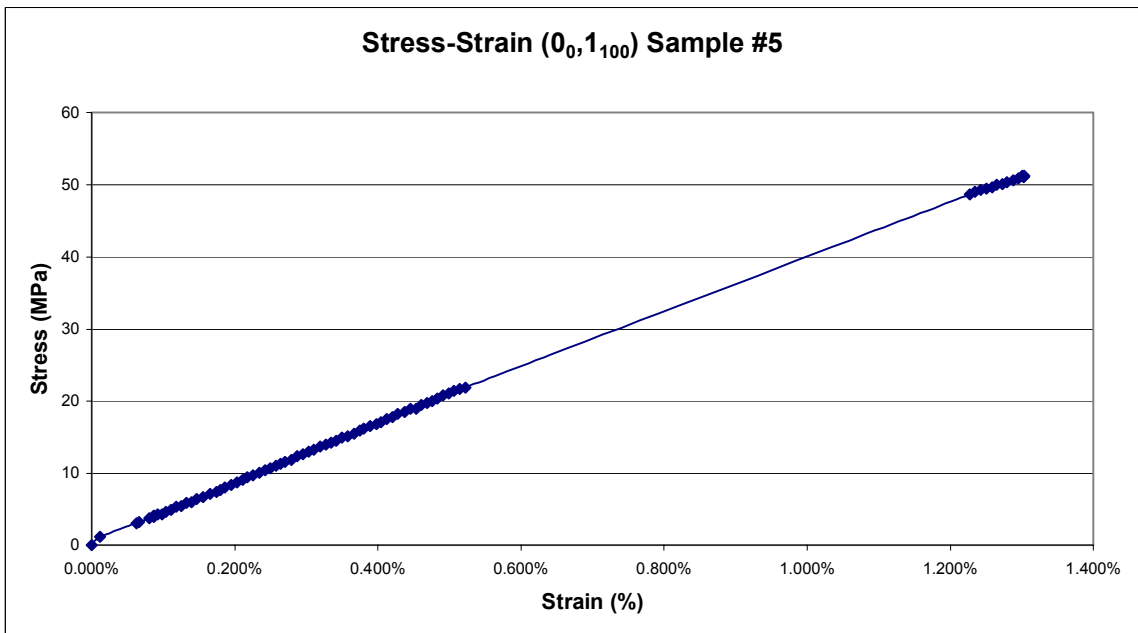
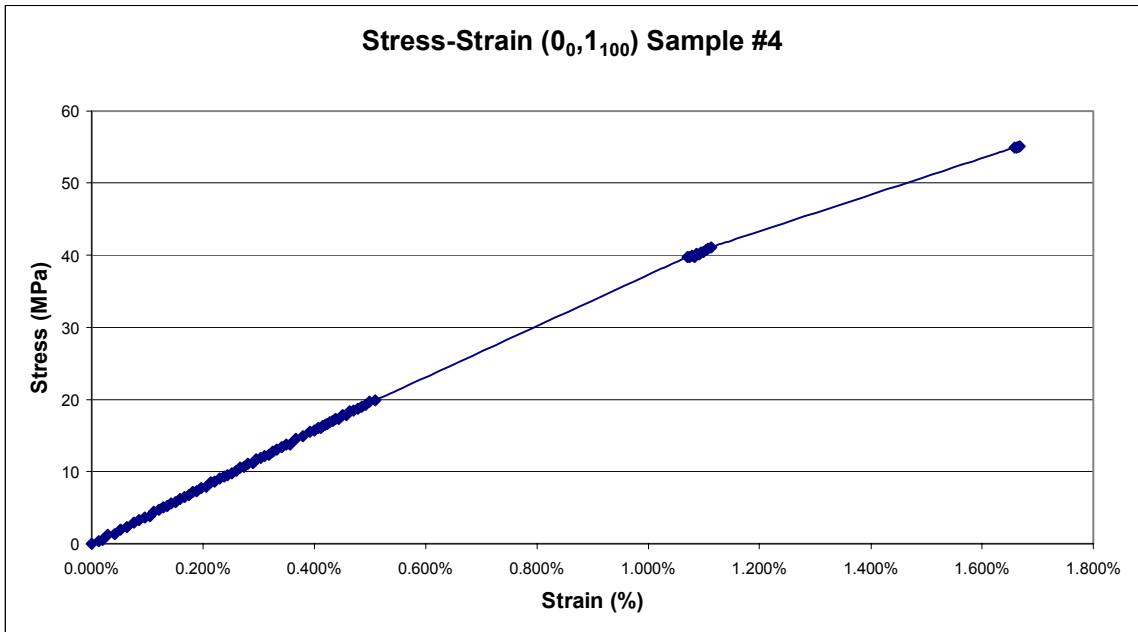


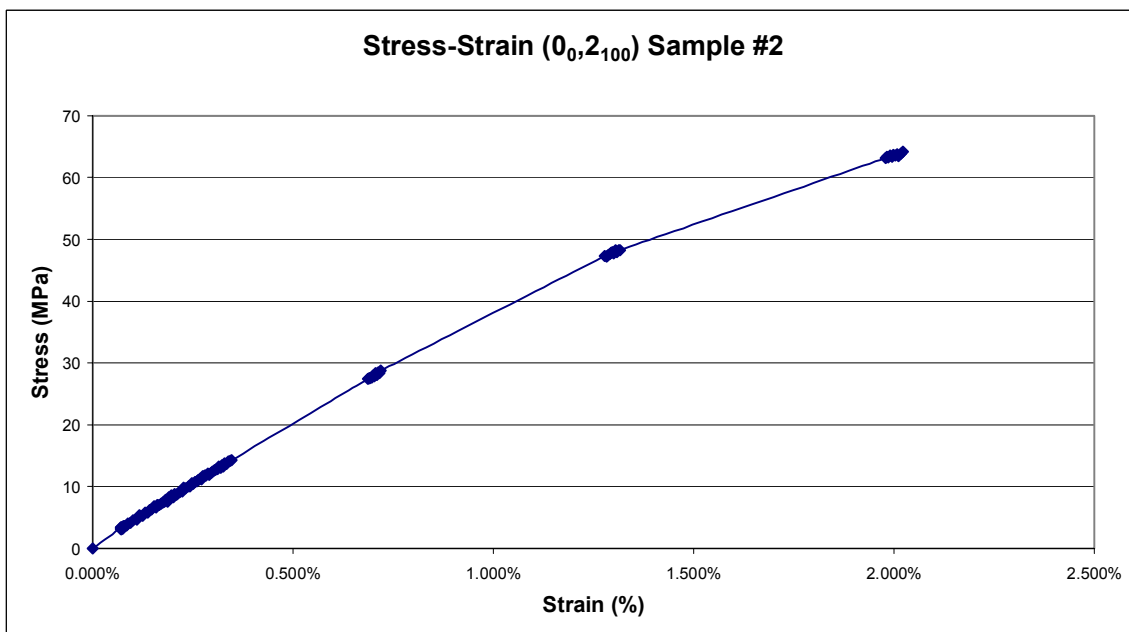
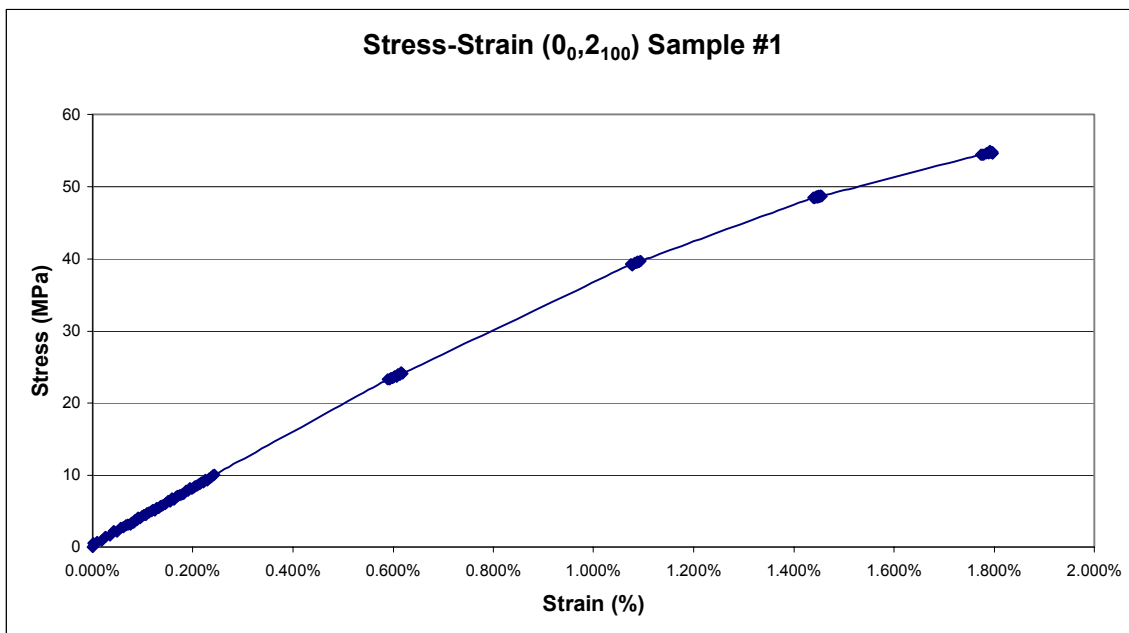


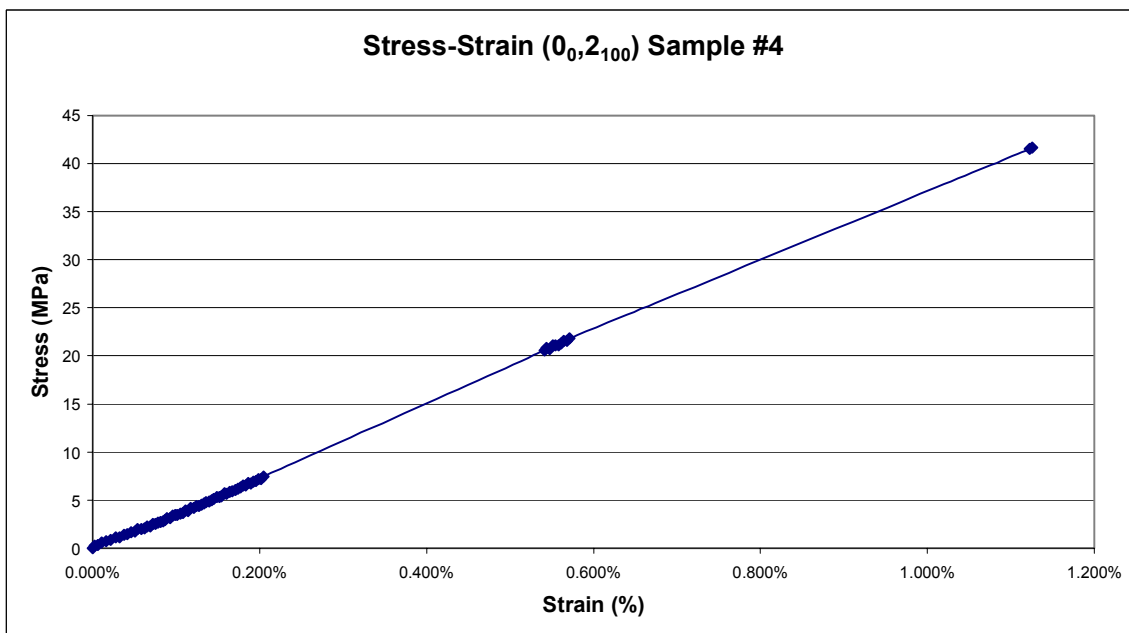
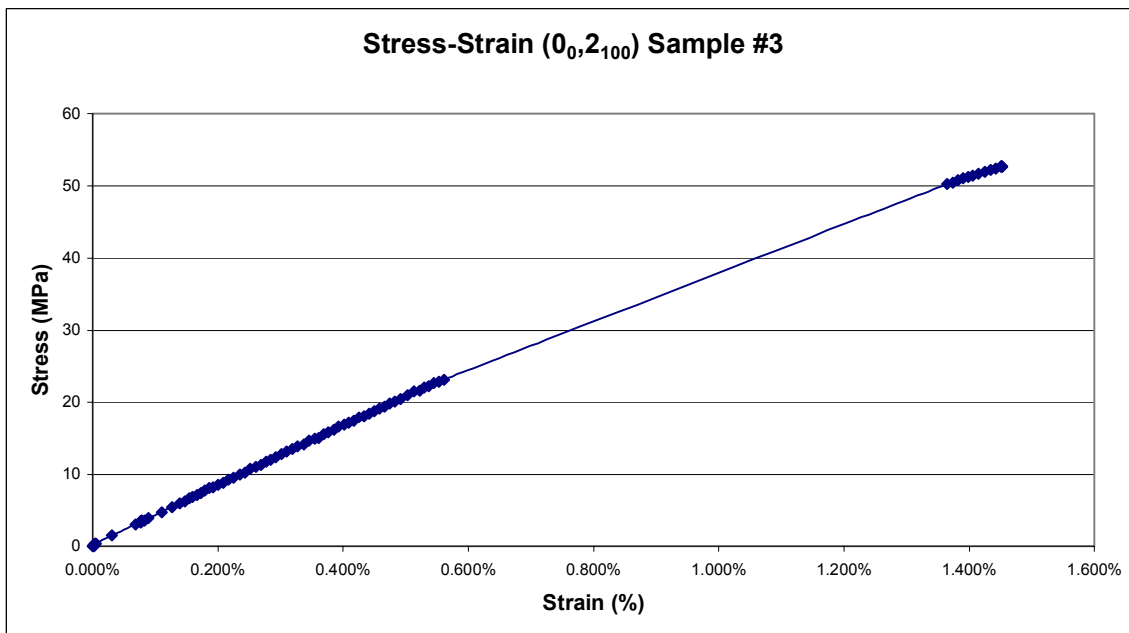
2.1.2 1st RG Curves

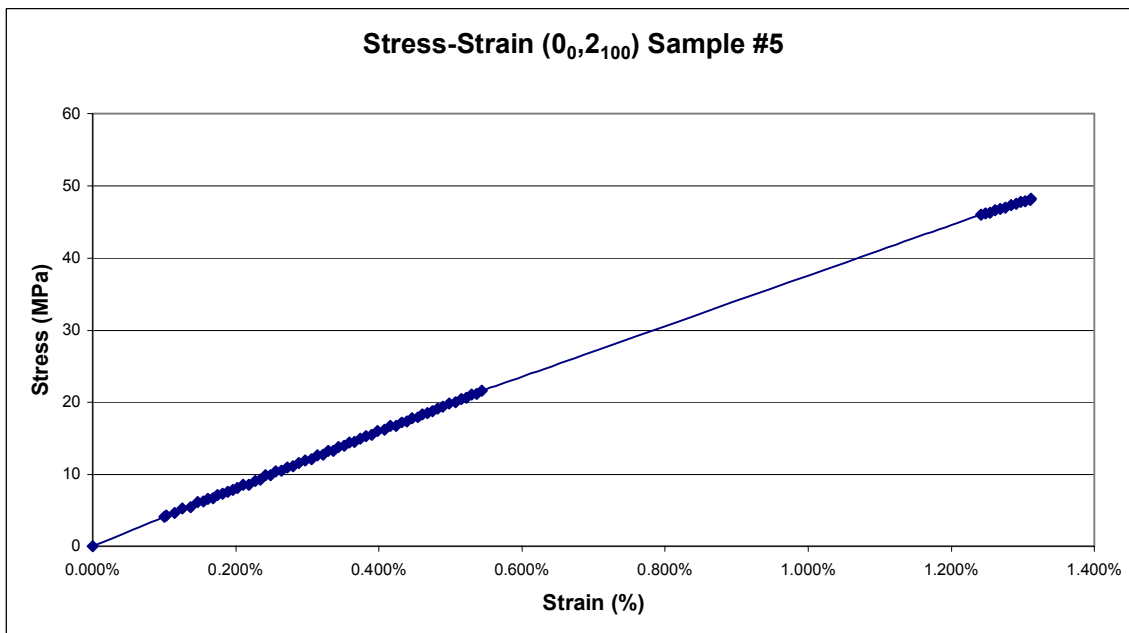




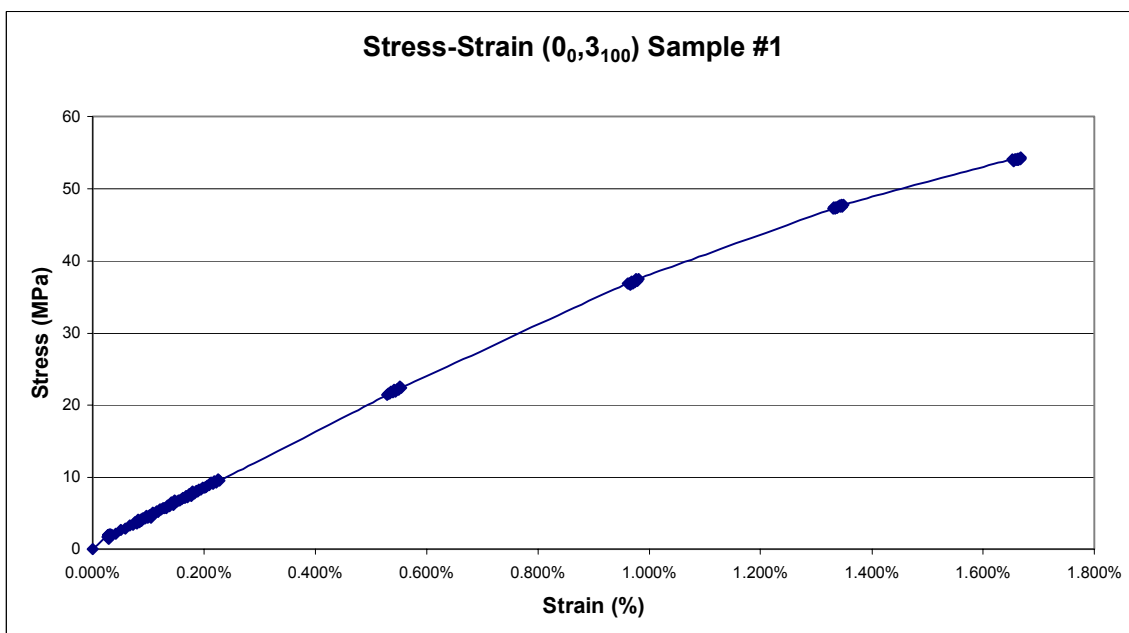


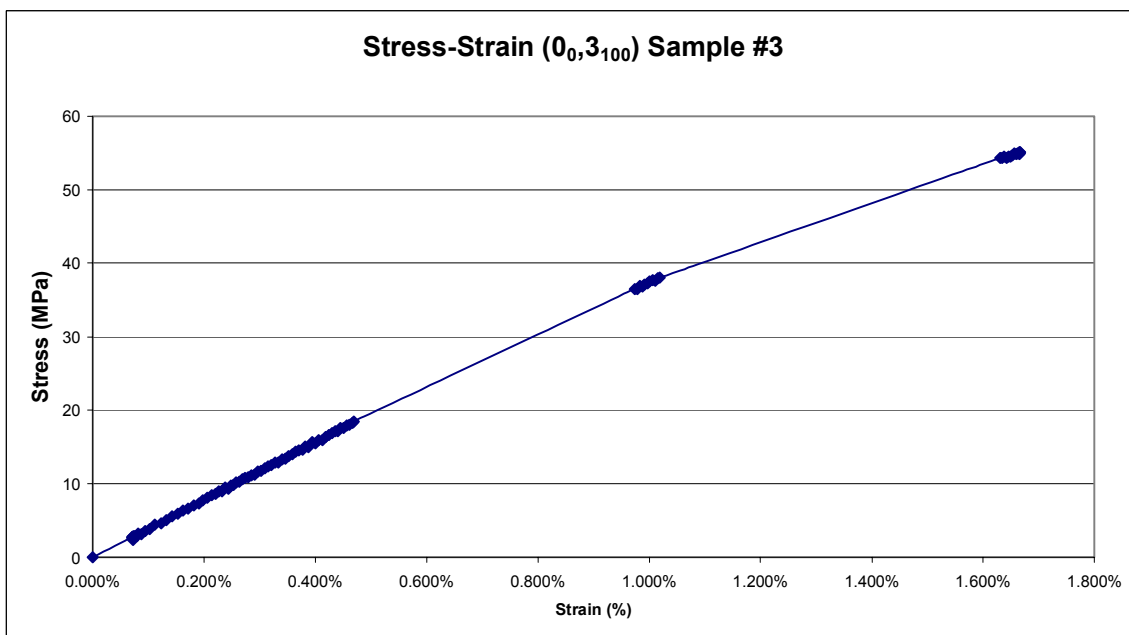
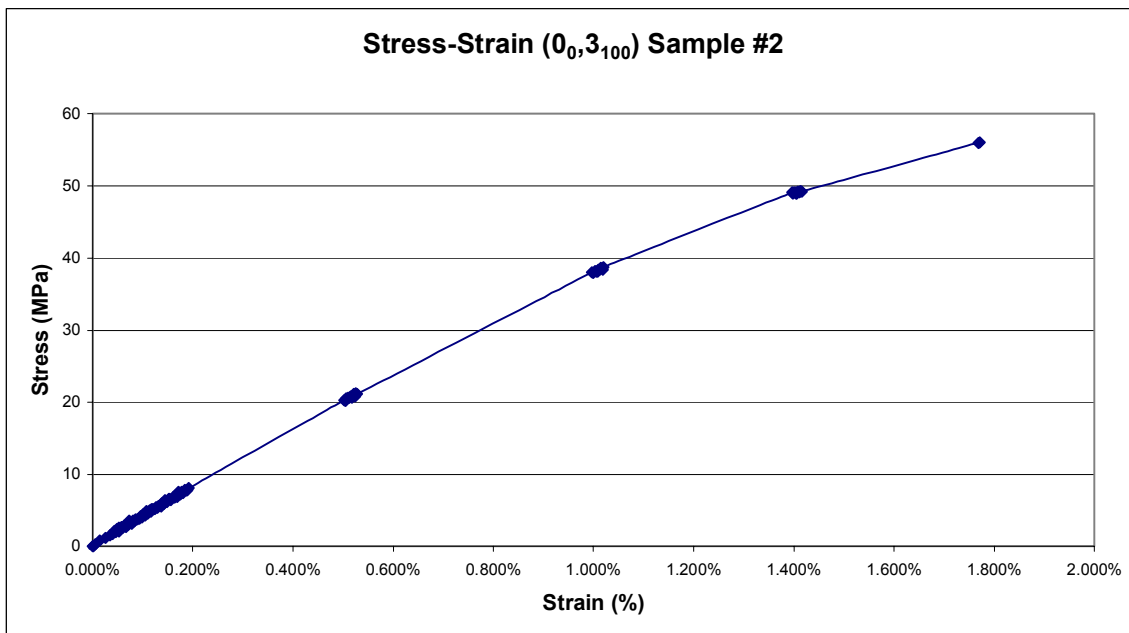
2.1.3 2nd RG Curves

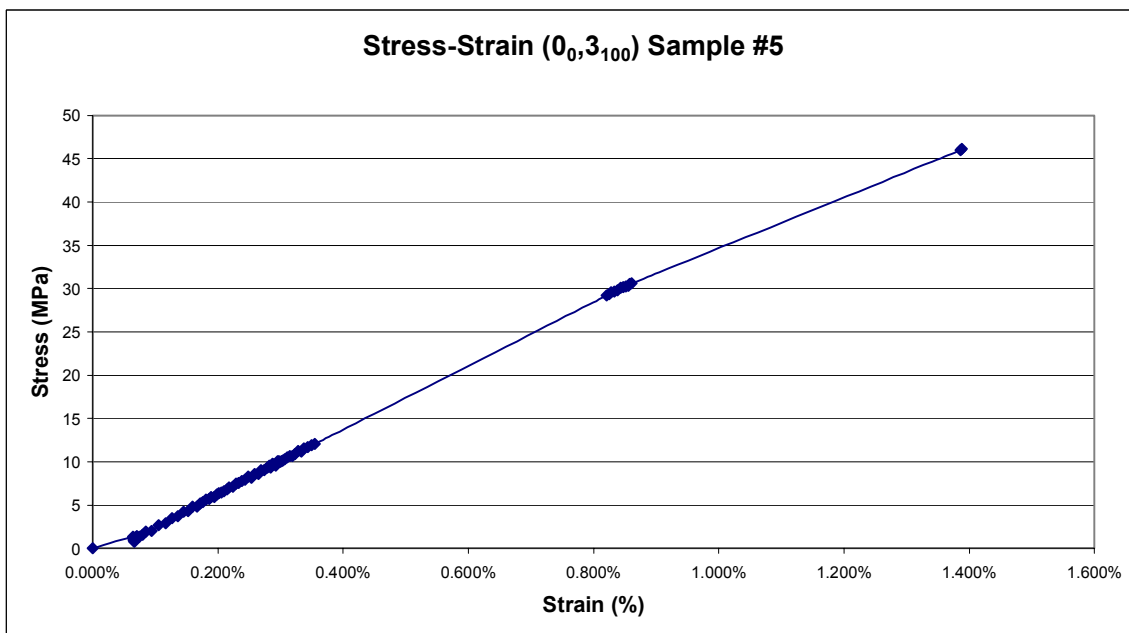
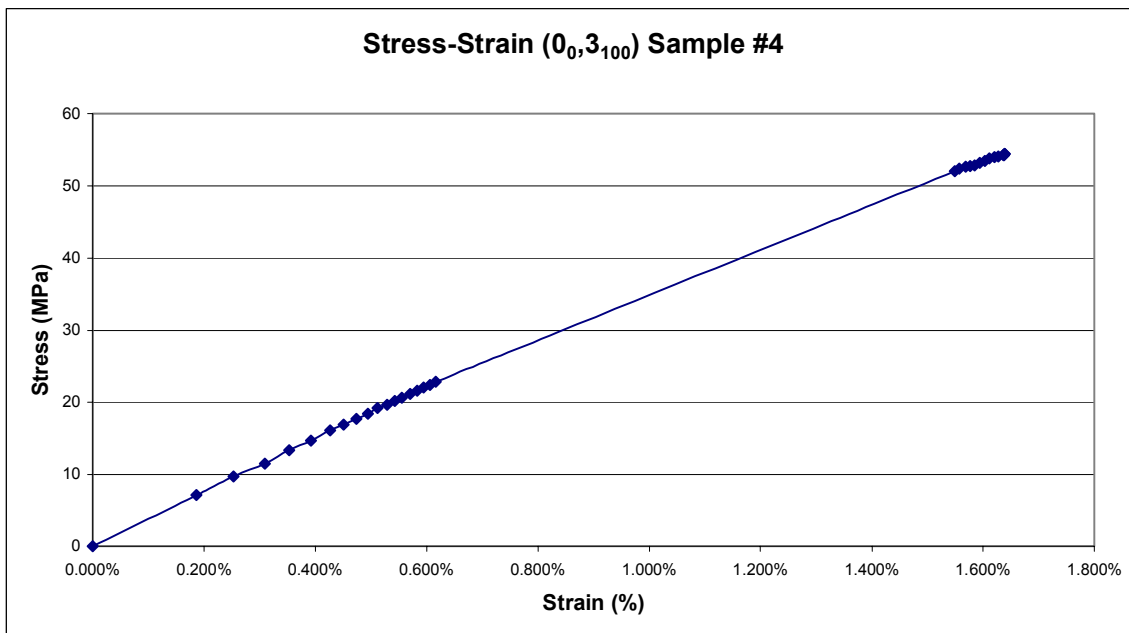


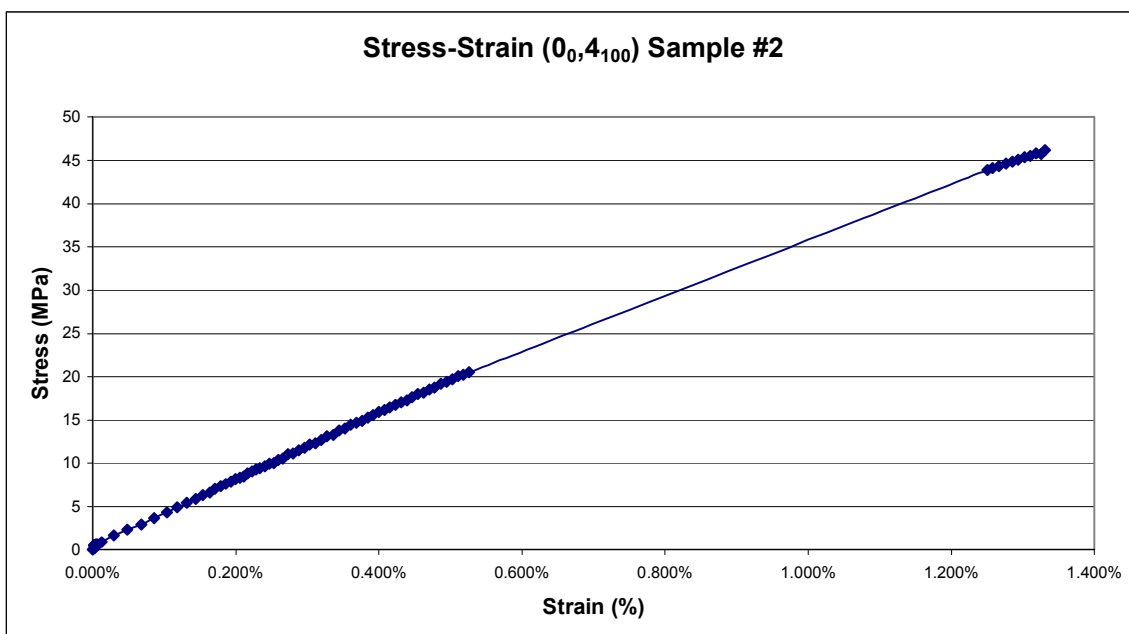
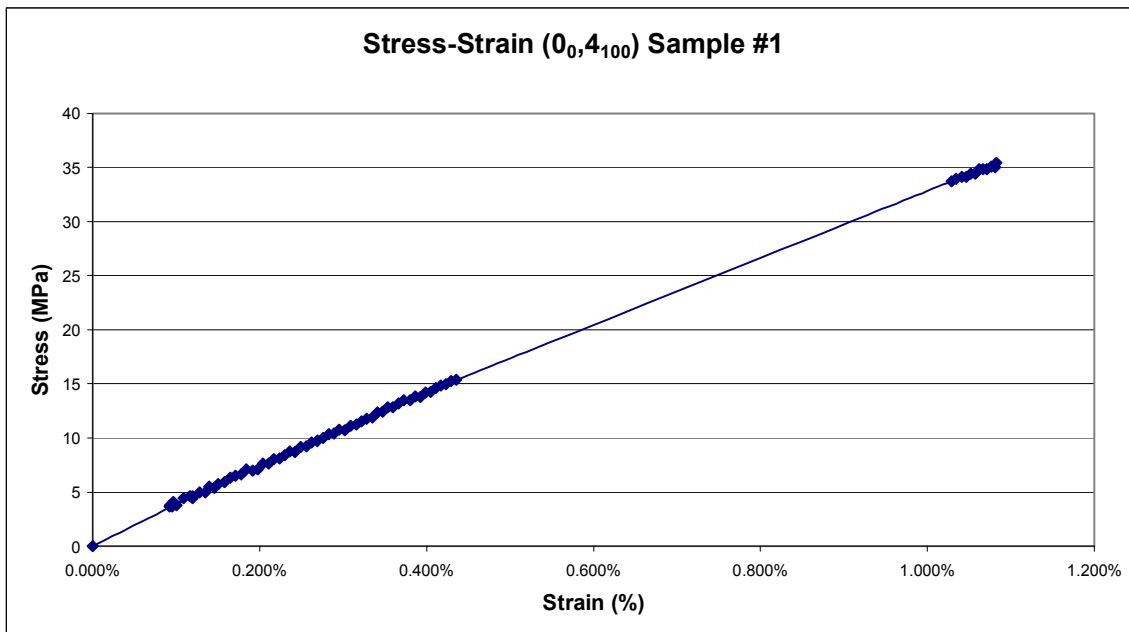


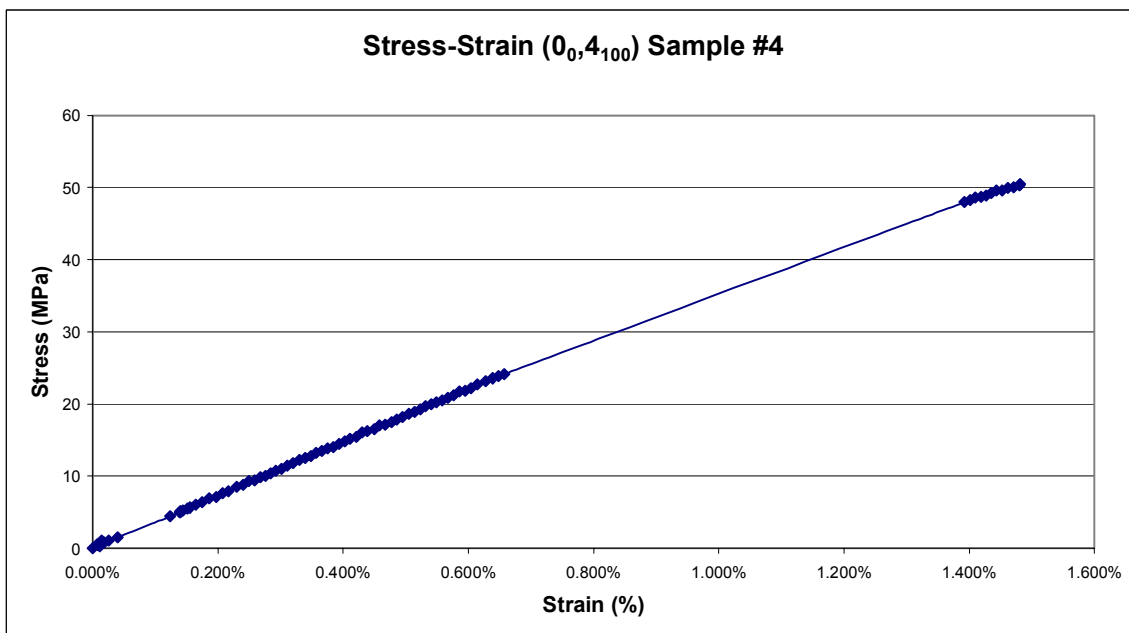
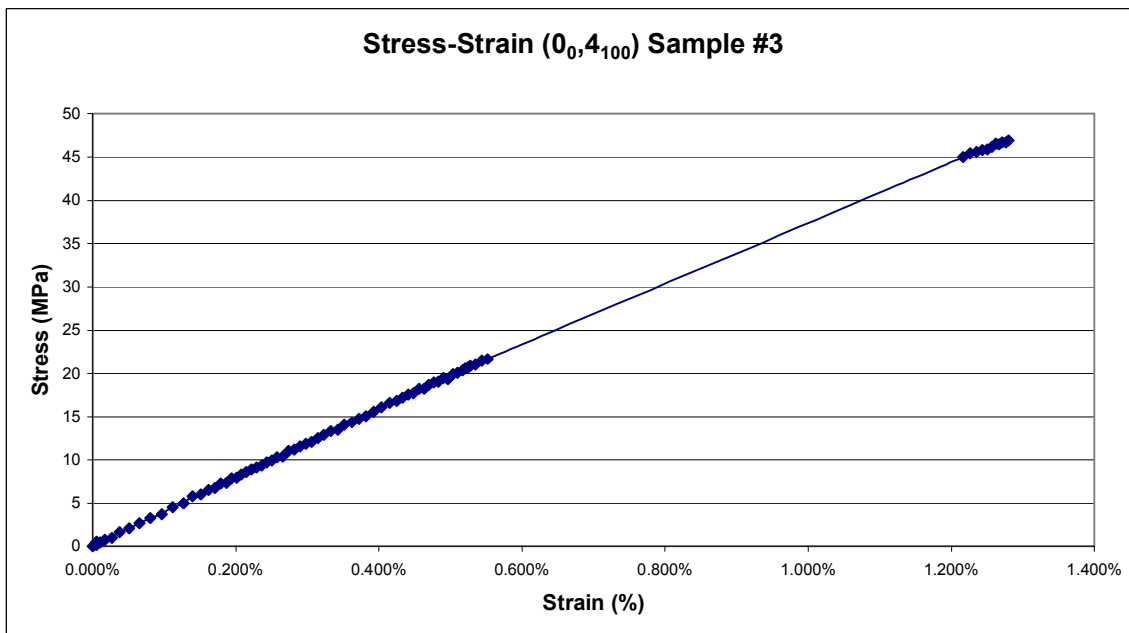
2.1.4 3rd RG Curves

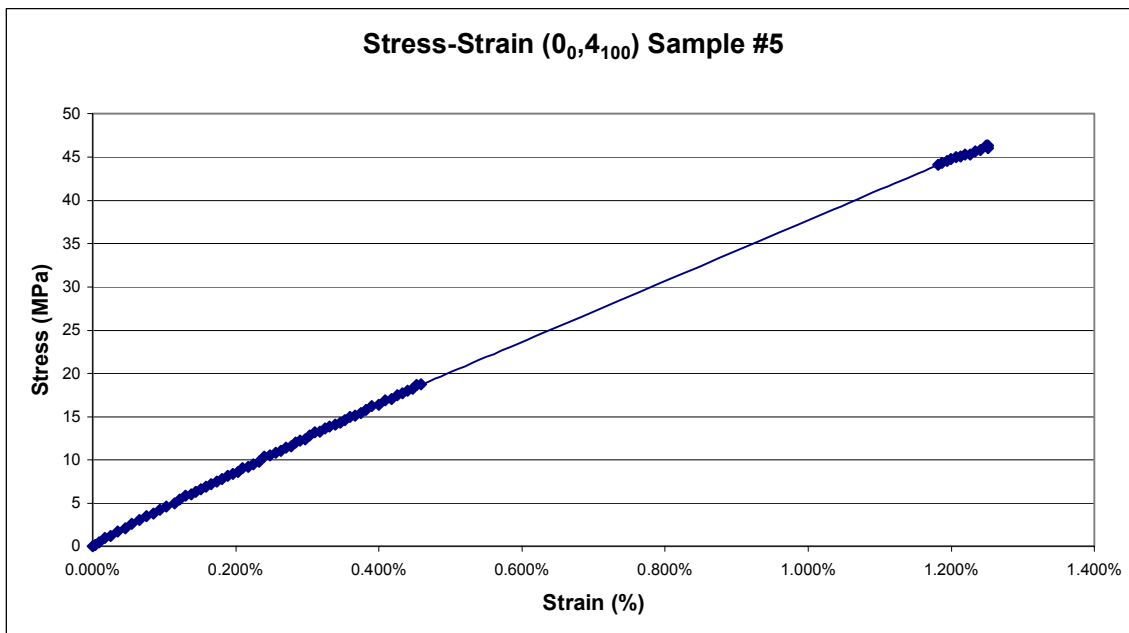




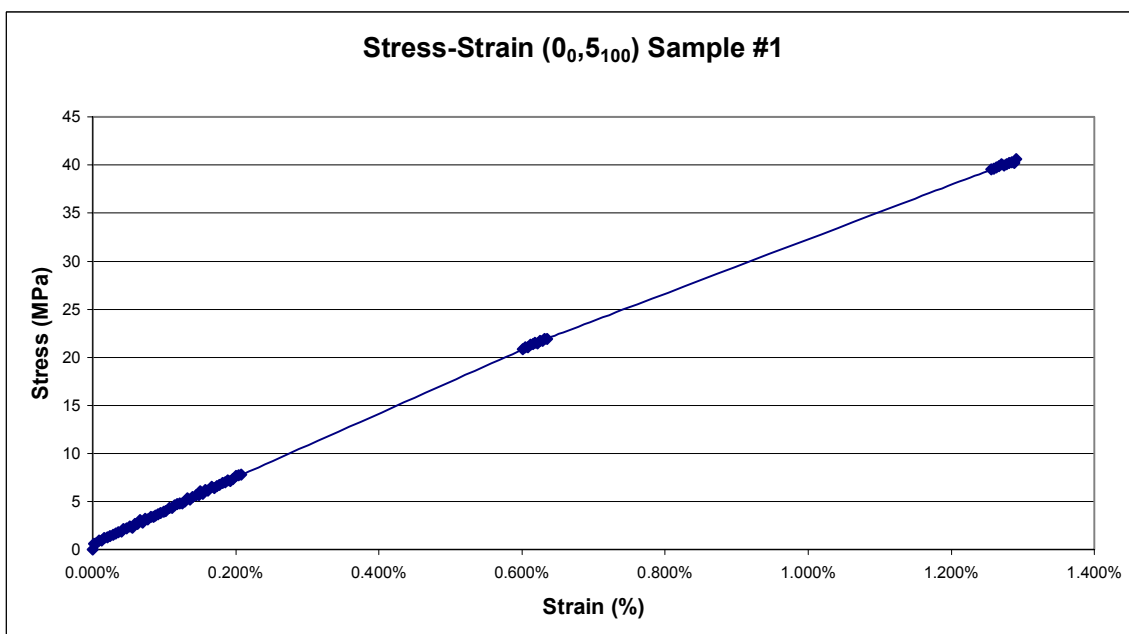


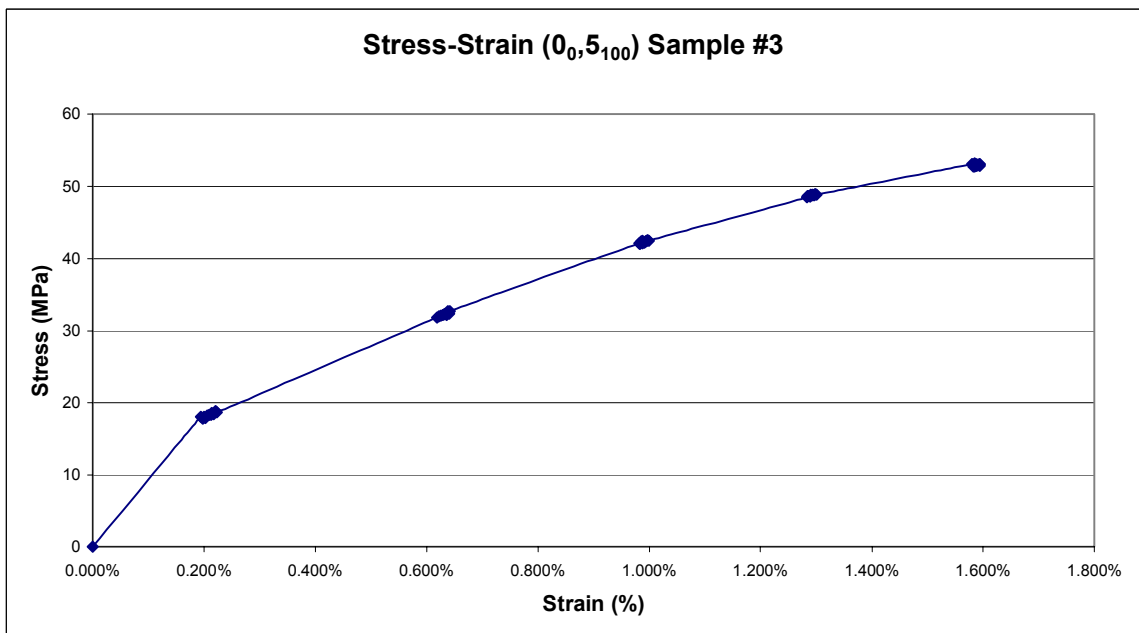
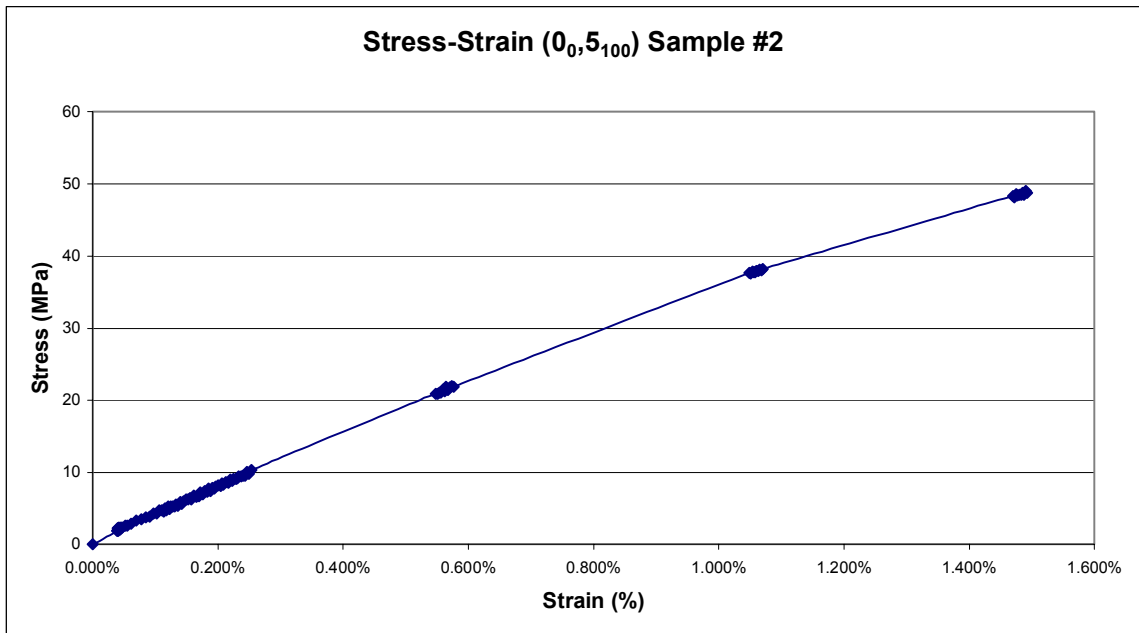
2.1.4 4th RG Curves

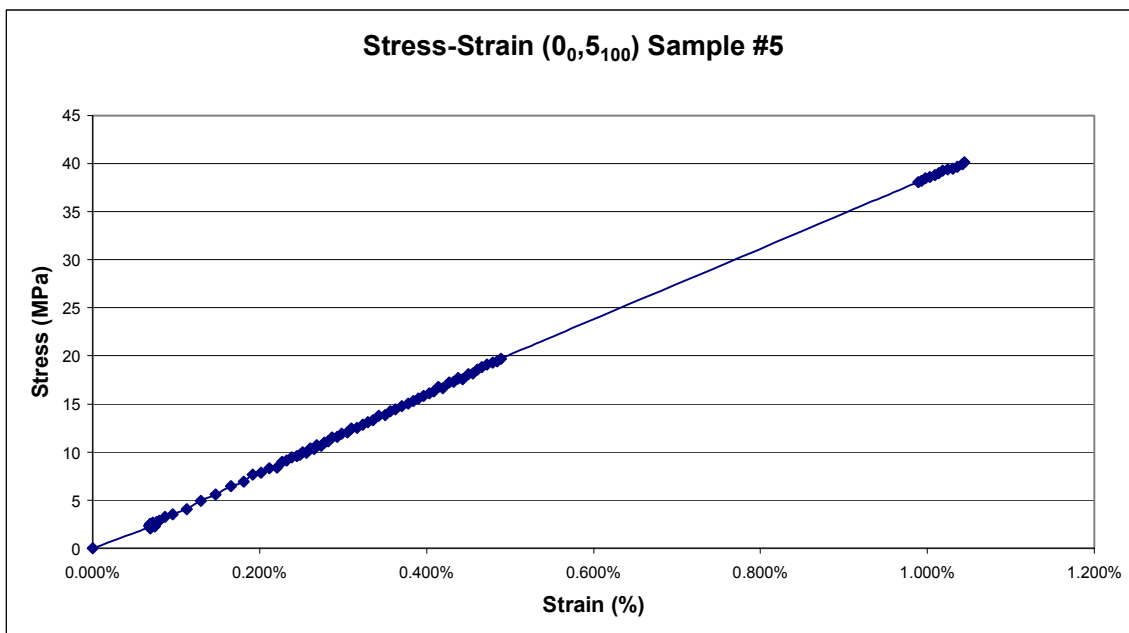
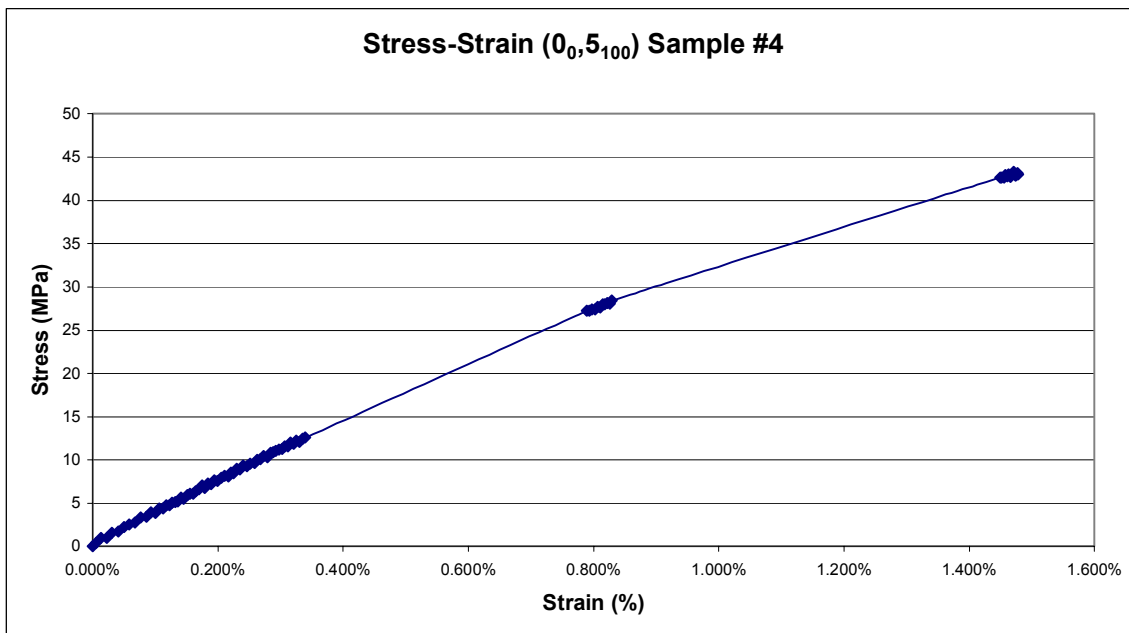




2.1.5 5th RG Curves

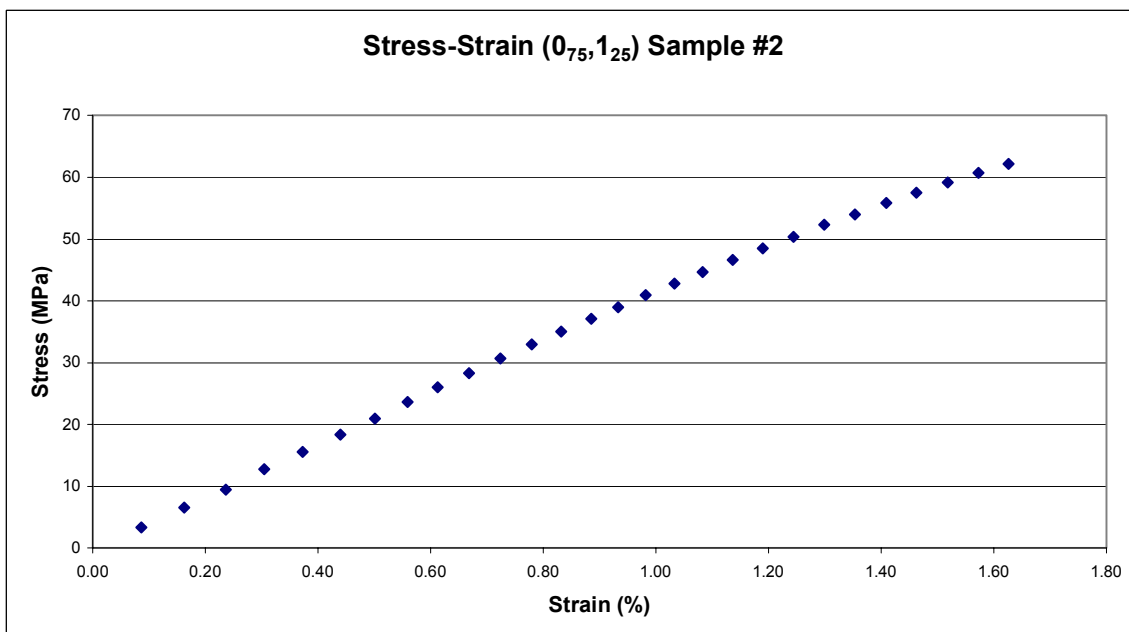
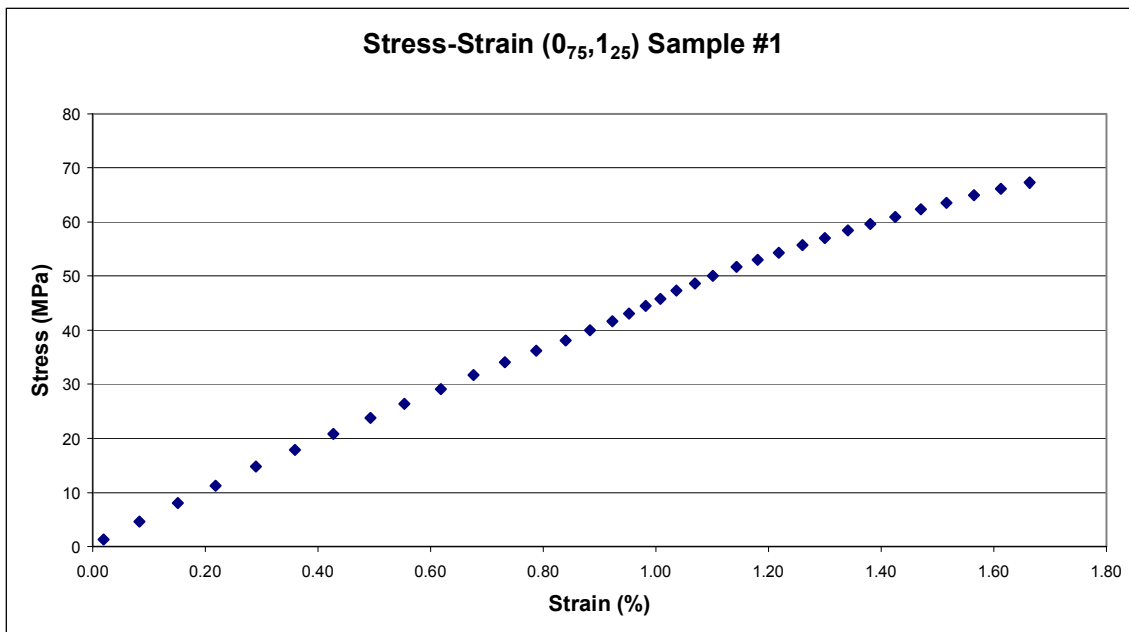


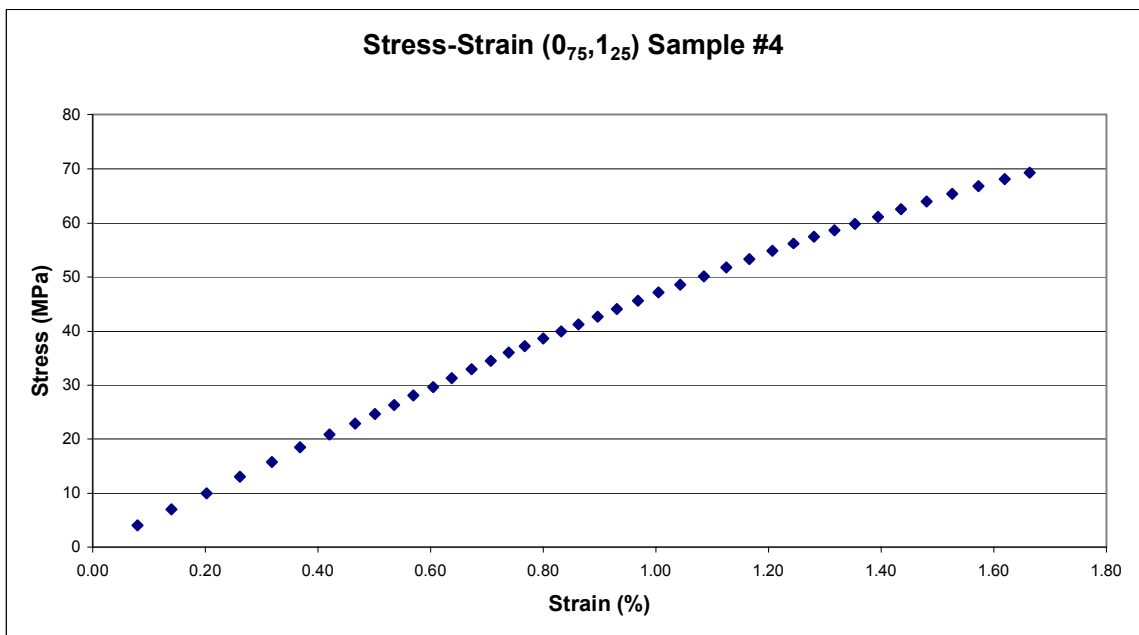
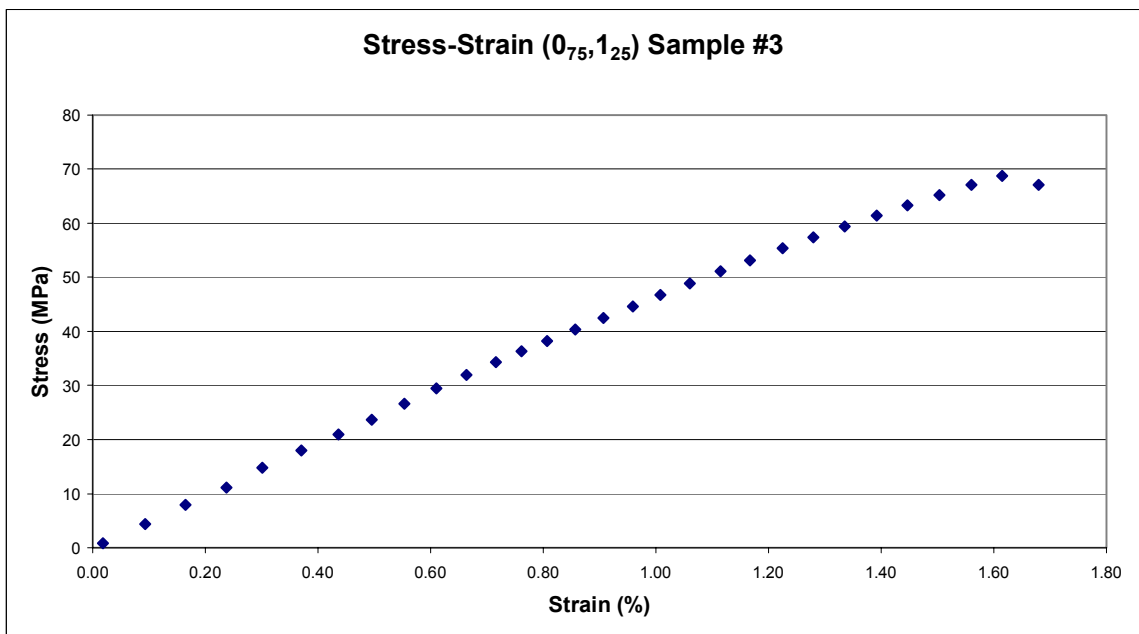


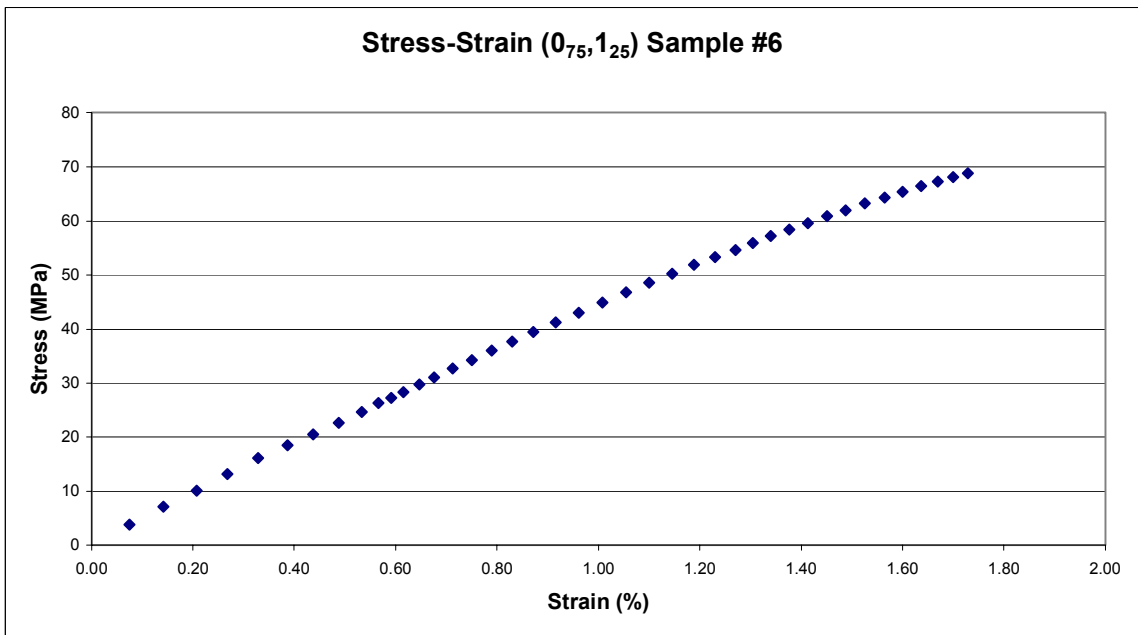
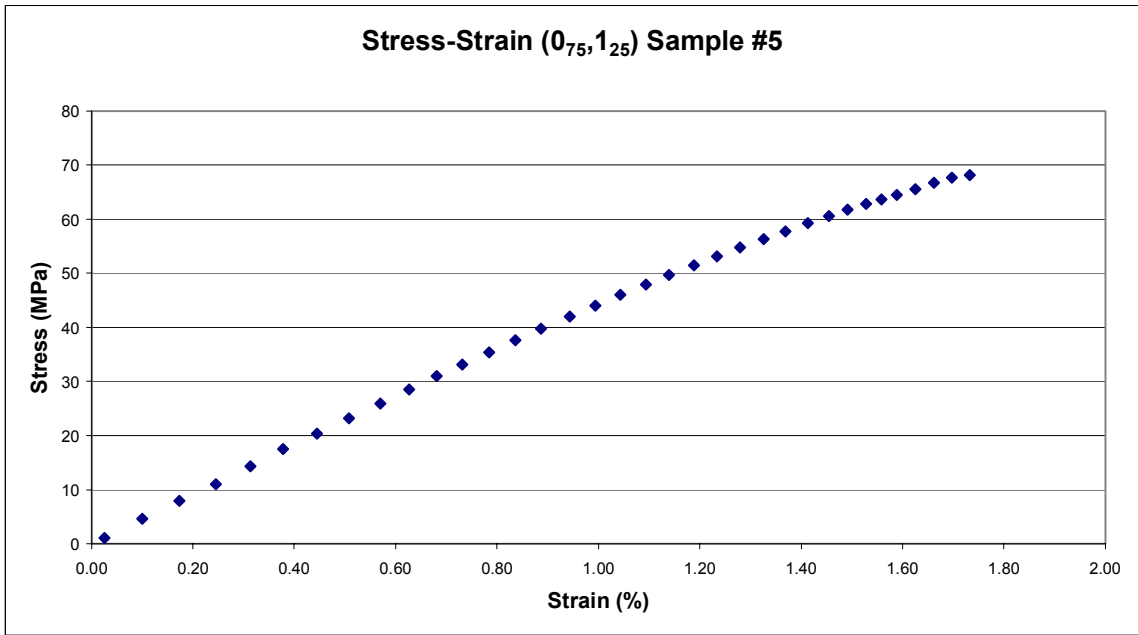


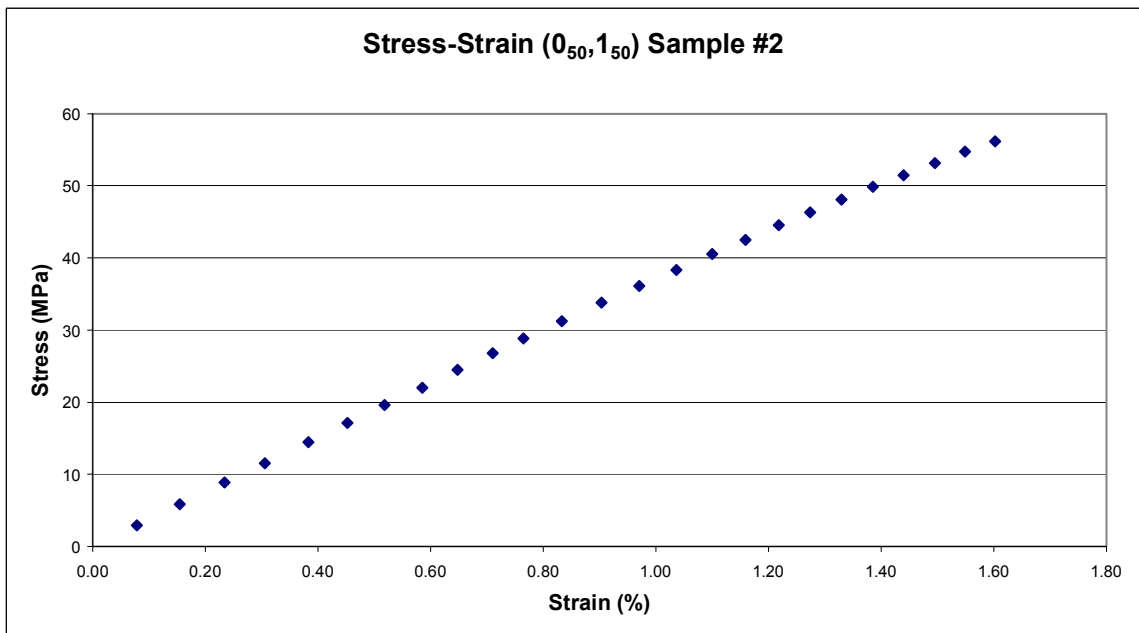
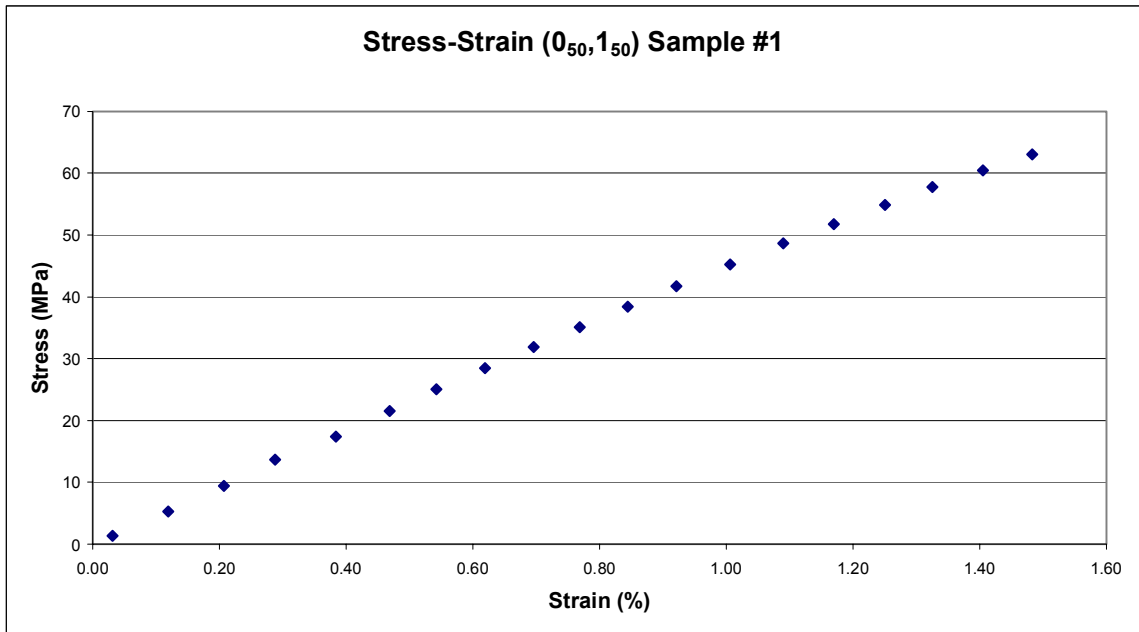
2.2 Various RG and RR

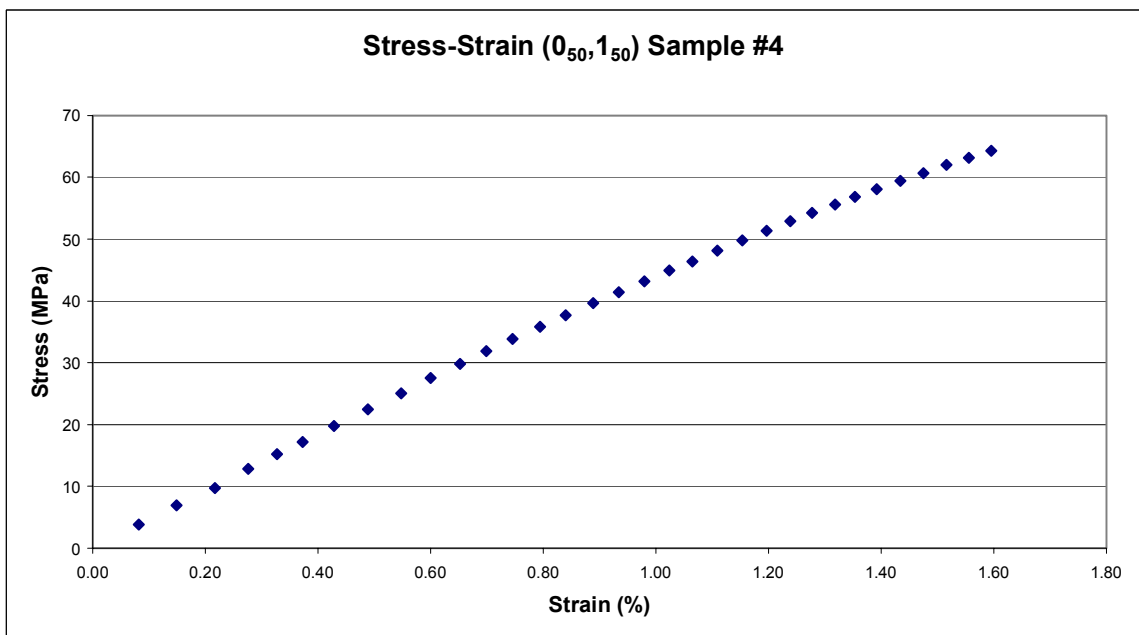
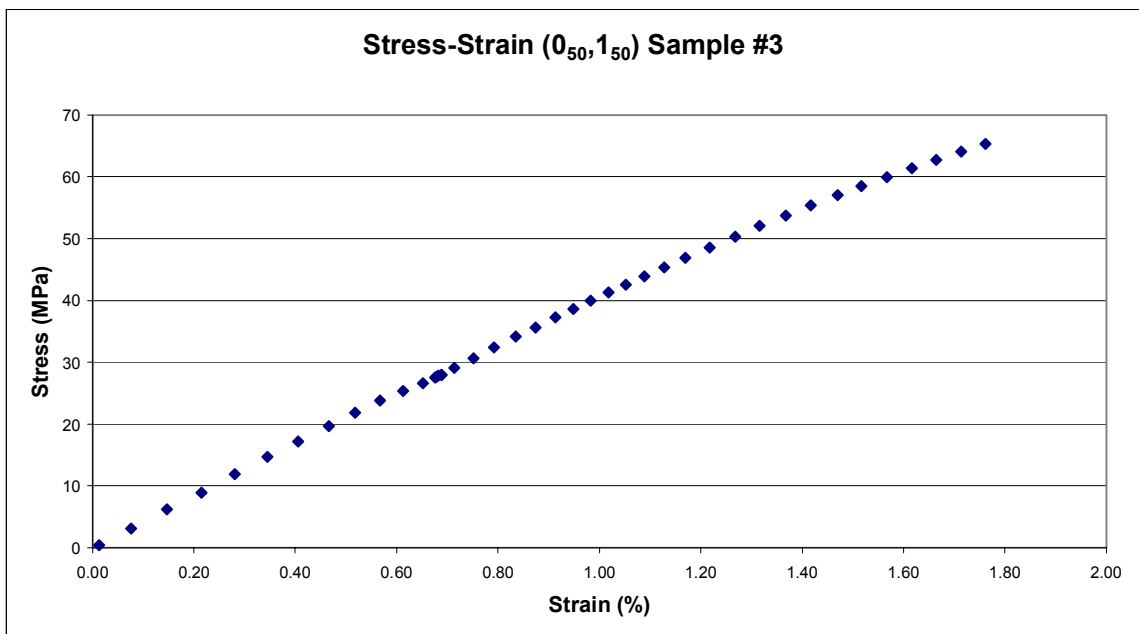
2.2.1 RG = 1st and RR = 25%

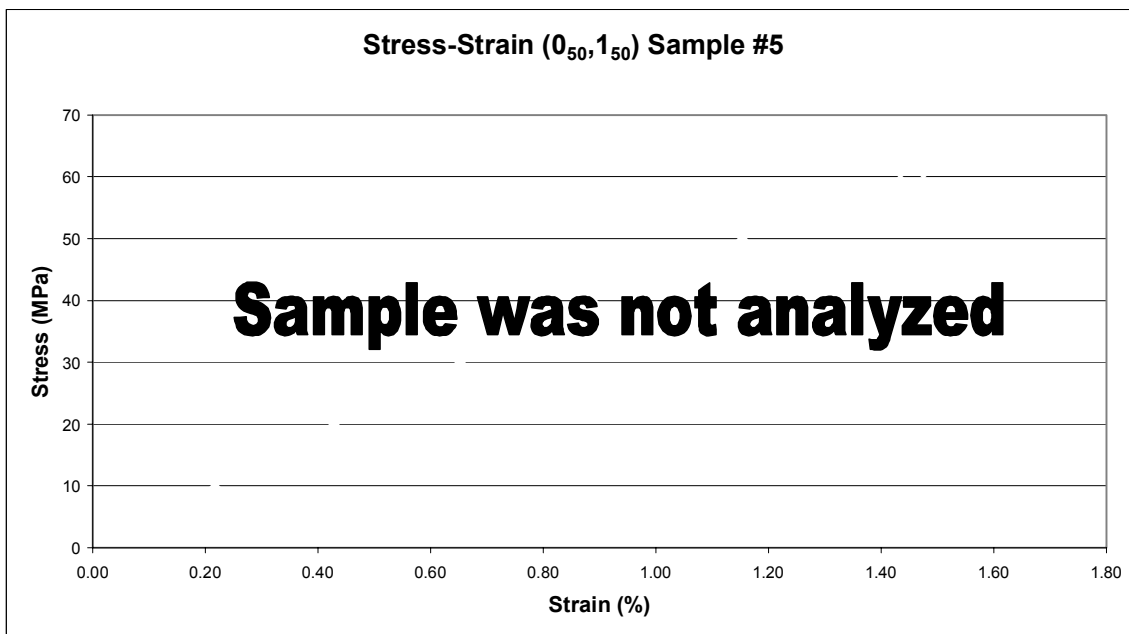




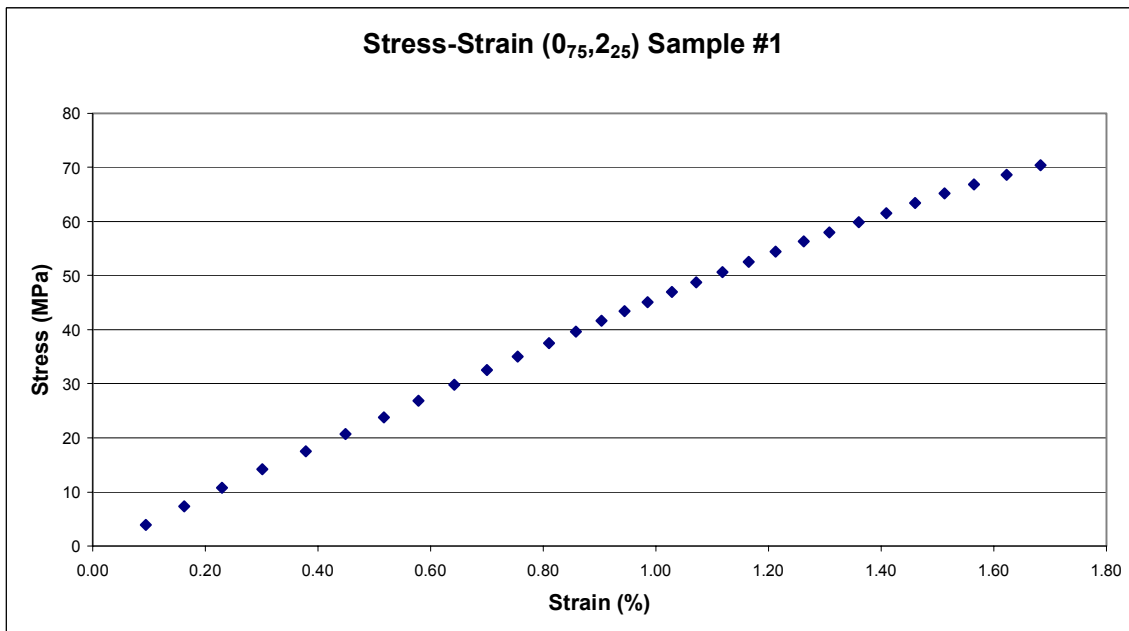


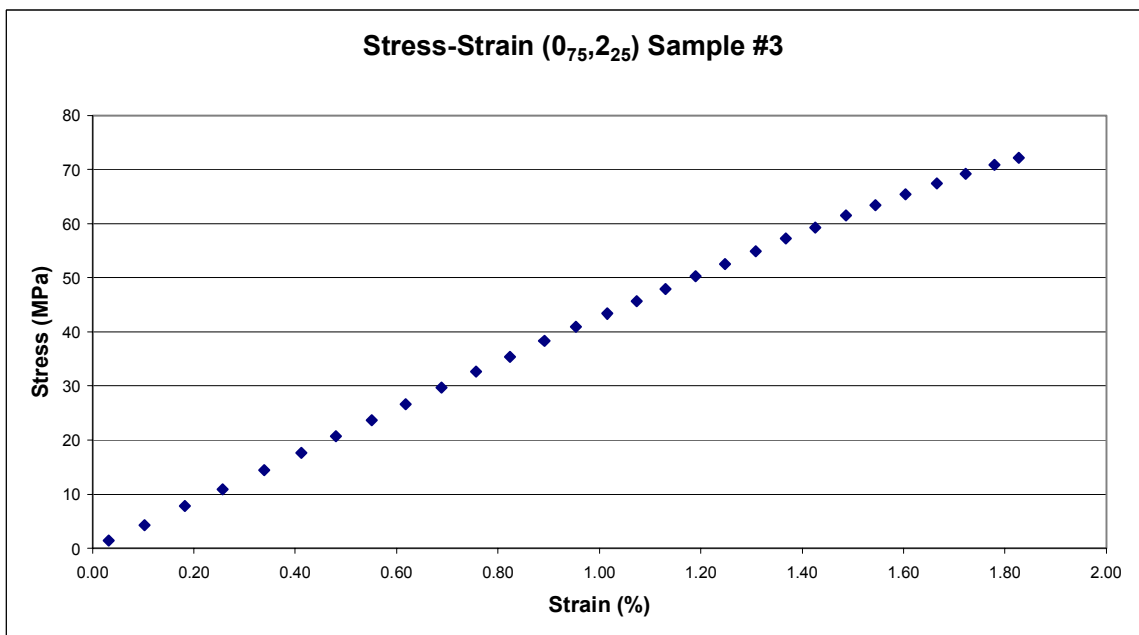
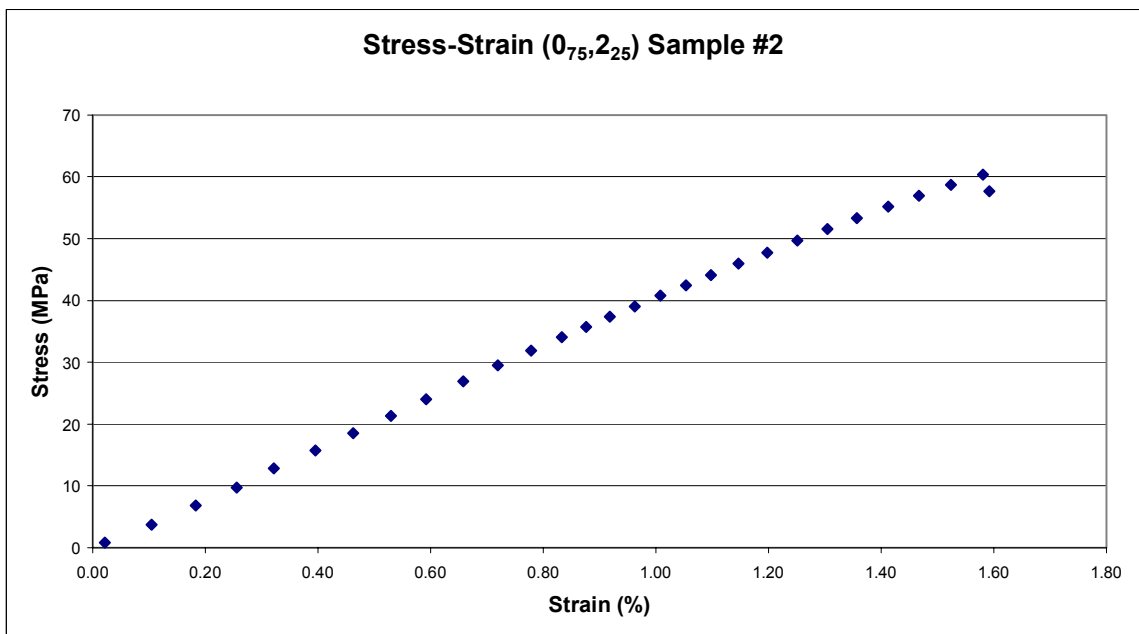
2.2.2 RG = 1st and RR = 50%

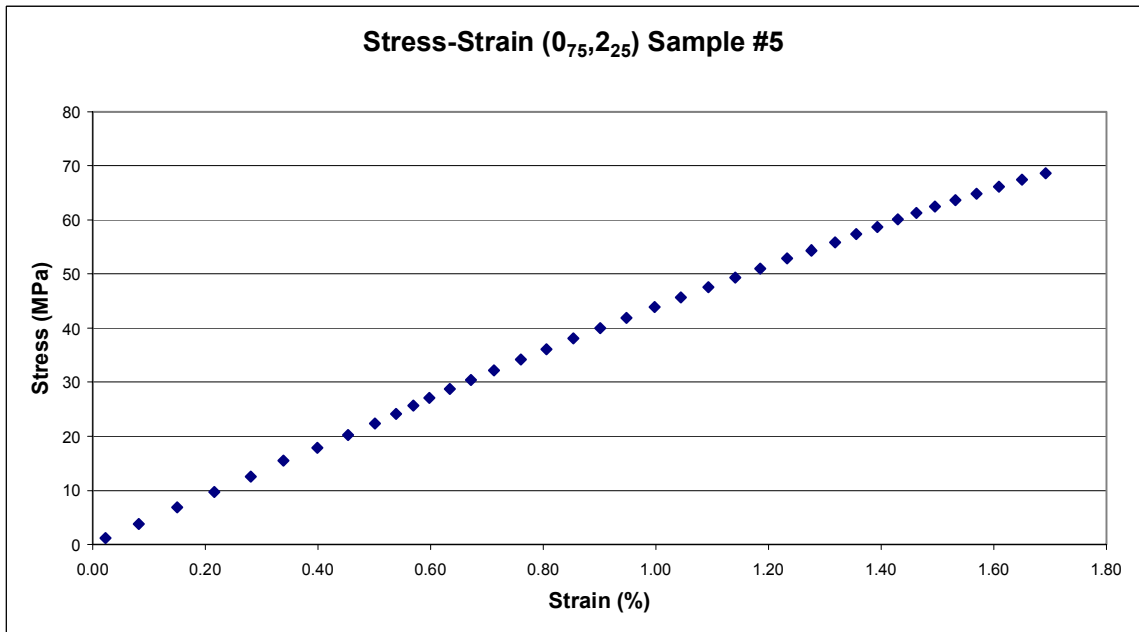
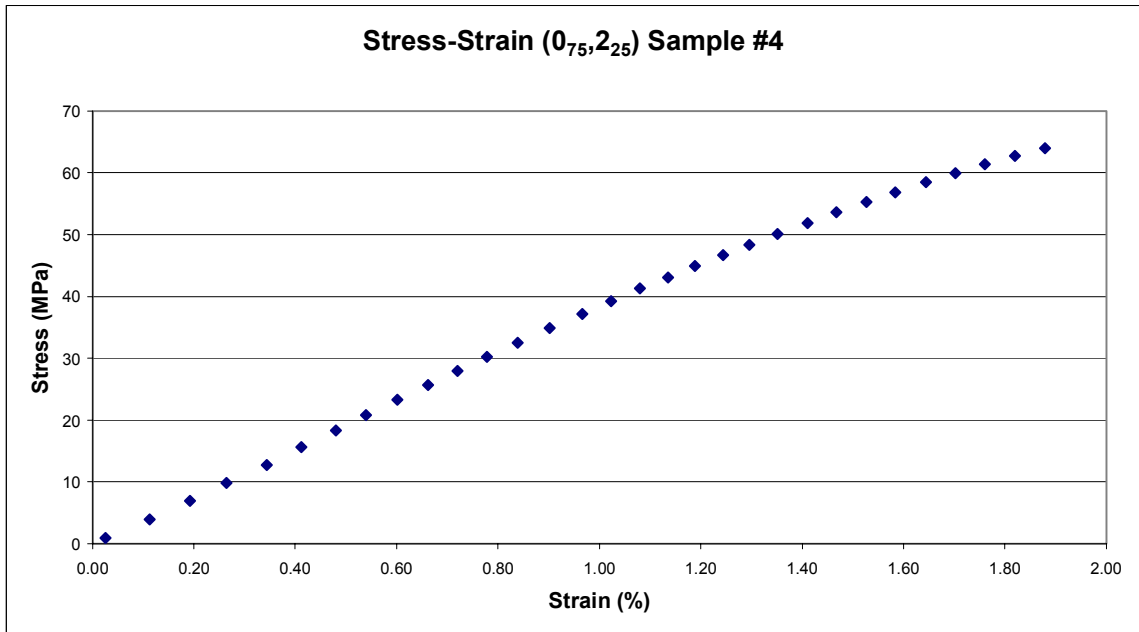




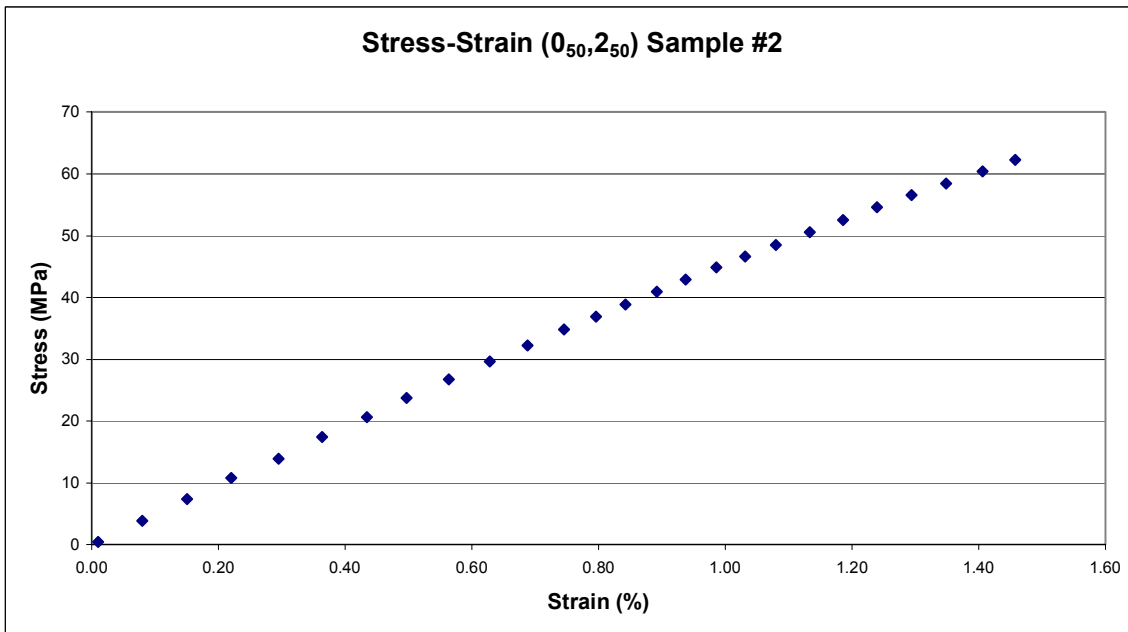
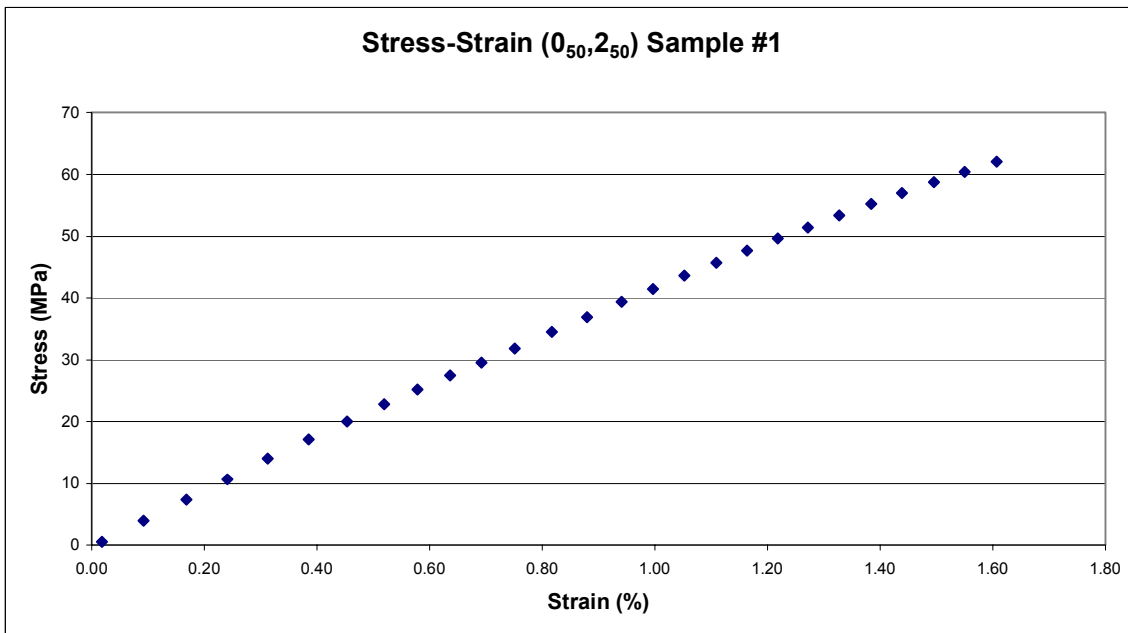
2.2.3 RG = 2nd and RR = 25%

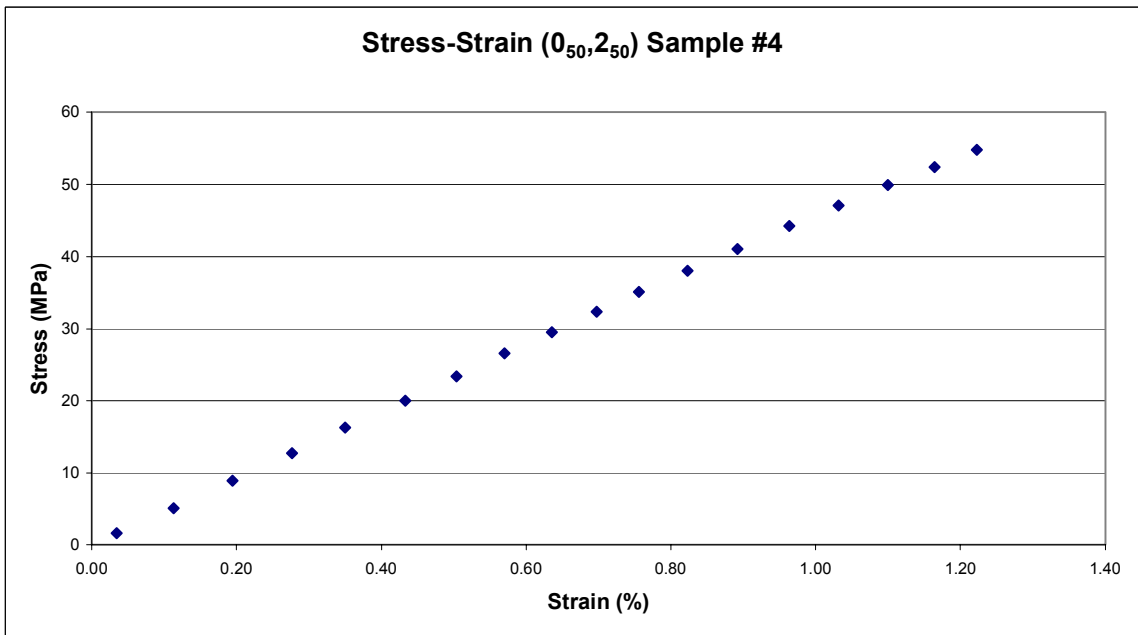
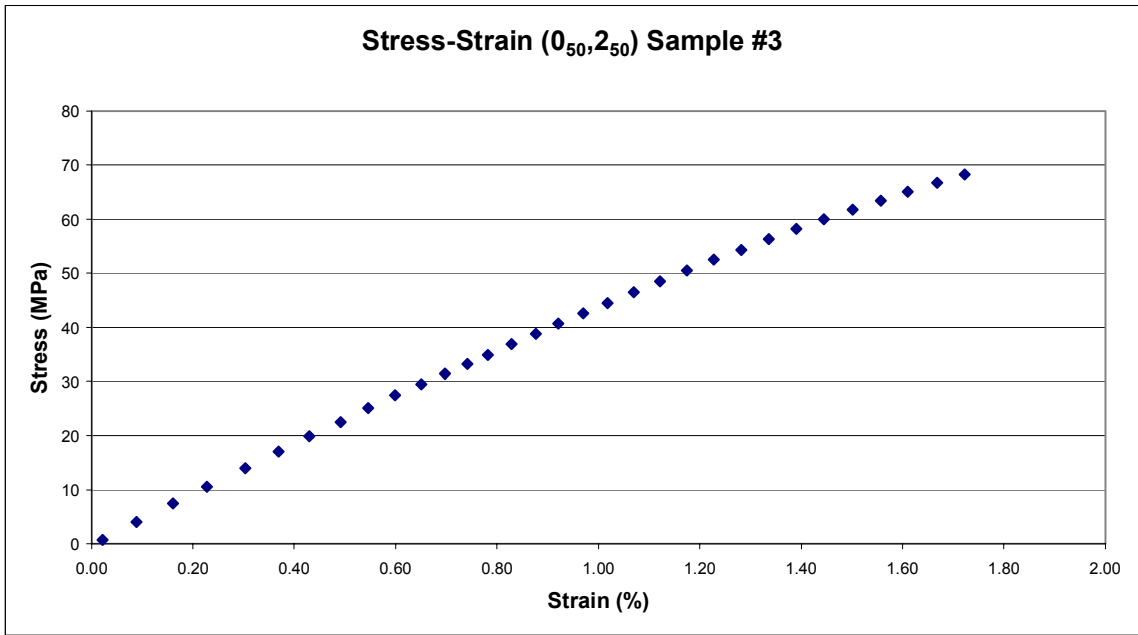


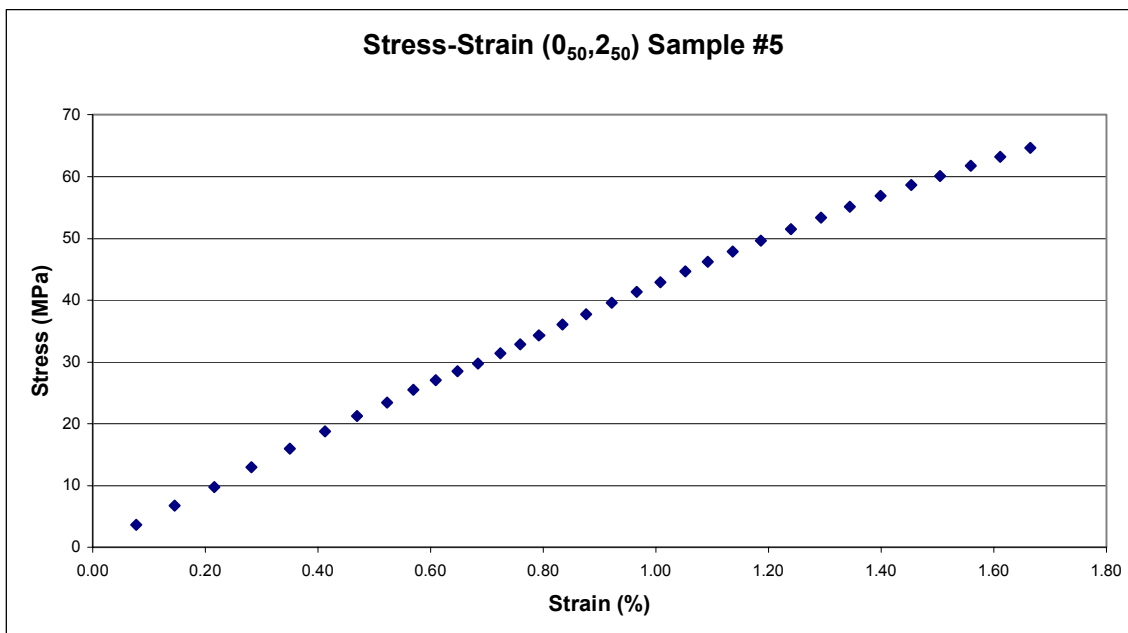




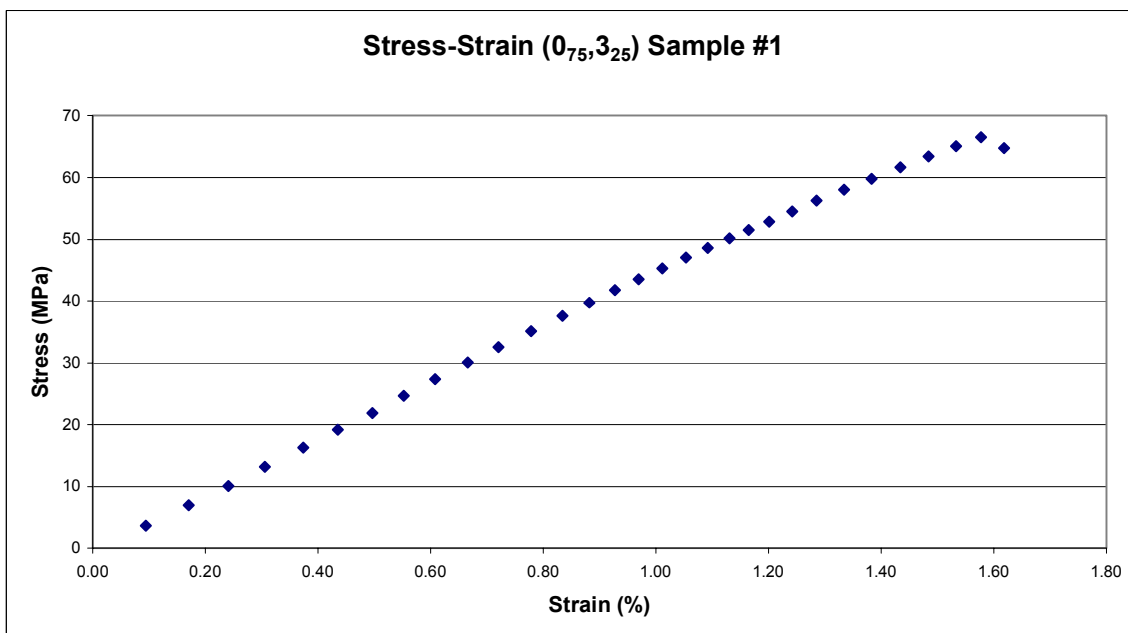
2.2.4 RG = 2nd and RR = 50%

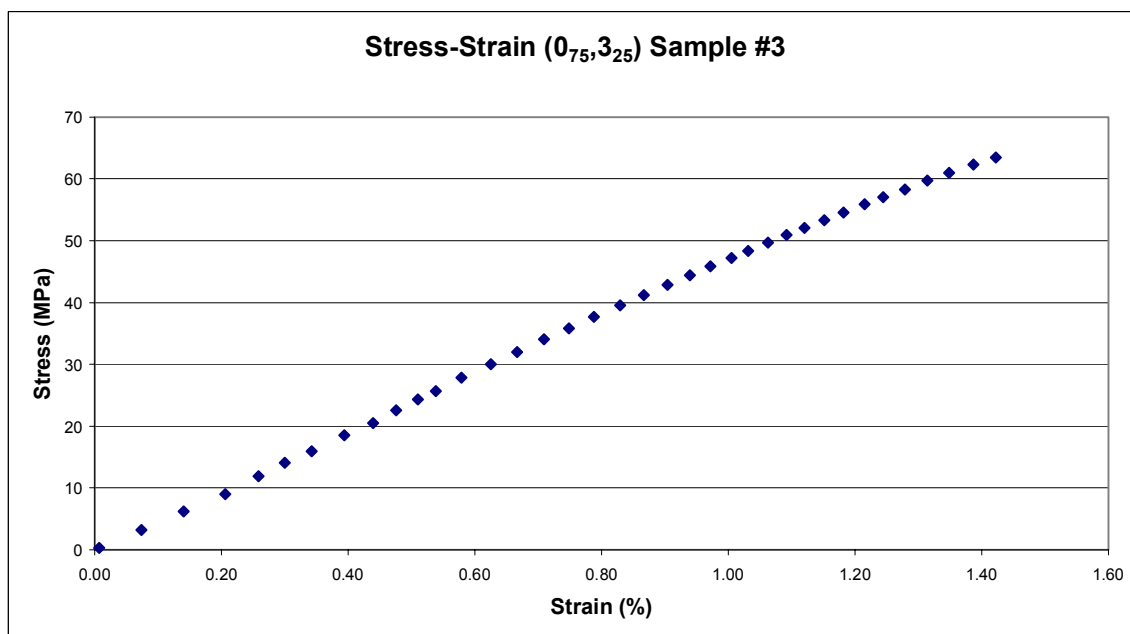
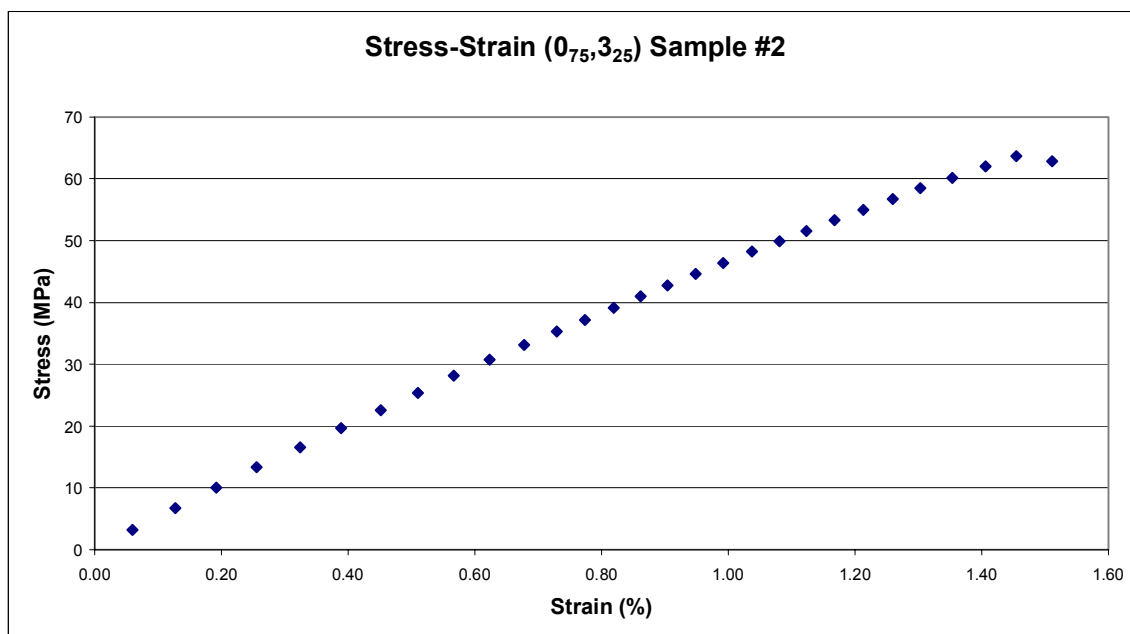


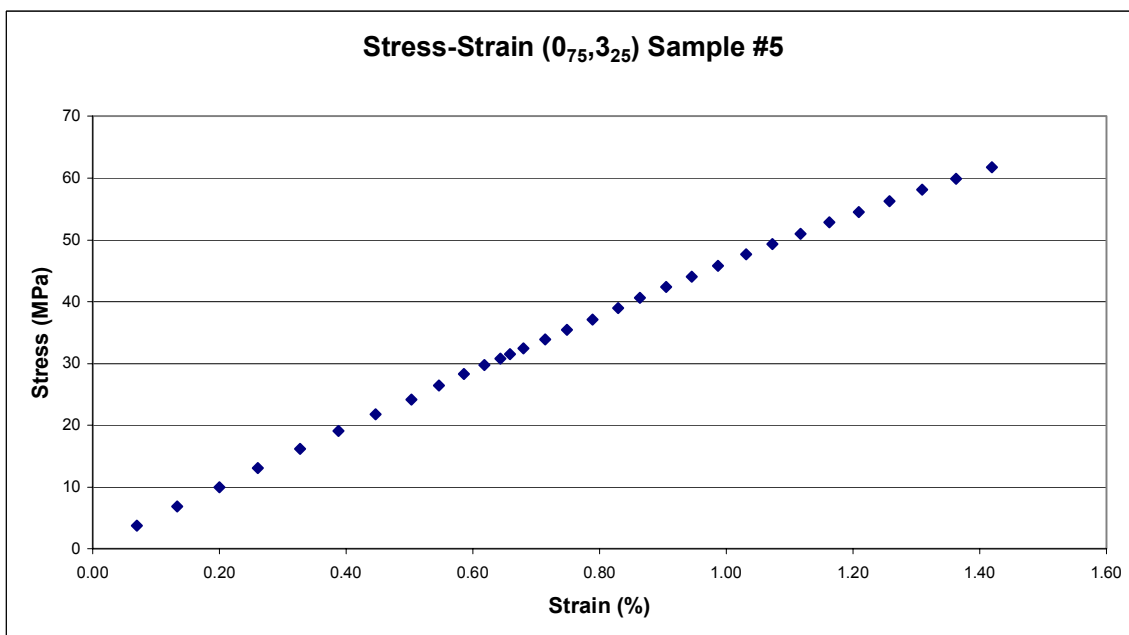
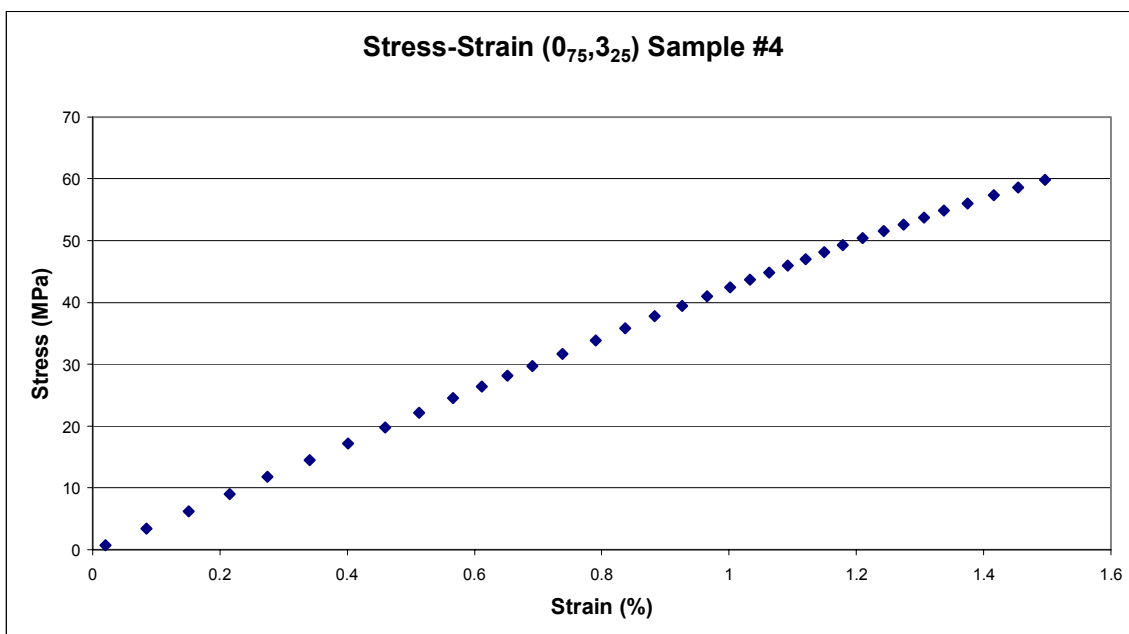




2.2.5 RG = 3rd and RR = 25%







2.2.6 RG = 3rd and RR = 50%