PROCESSING AND CHARACTERIZATION OF POLY(ETHYLENE TEREPHTHALATE) BASED COMPOSITES

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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ABSTRACT

PROCESSING AND CHARACTERIZATION OF POLY(ETHYLENE TEREPHTHALATE) BASED COMPOSITES

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Polymeric composites are any of the combinations or compositions that comprise two or more materials as separate phases, at least one of which is a polymer. By mixing a polymer with another material, such as glass, carbon, or another polymer, it is often possible to improve the desired properties of the polymer.

In this study, ternary composites were prepared by using recycled poly(ethylene terephthalate), PET as the matrix material, short glass fiber (SGF) as the reinforcing filler and thermoplastic elastomer as the impact modifier. Bottle grade recycled PET was mixed in a twin screw extruder with a thermoplastic elastomer which is a terpolymer of ethylene/methyl acrylate/glycidyl methacrylate (E-MA-GMA), and E type short glass fiber is fed to the extruder from a side feeder. During this study, recycled PET was mixed with from 10 to 50 wt. % elastomer, and SGF was added to the system in the range from 10 to 40 % by weight. Processing parameters were kept constant during extrusion. The composites were then compression molded for characterization experiments.

The produced composites were characterized in terms of their mechanical and thermal properties and morphologies. Melt behavior and fiber length distribution of the composites were also determined for selected composites. In ternary systems with 10 % elastomer, highest tensile strength values were observed. High tensile and flexural moduli values were obtained for the composites containing 20 % elastomer. Results of impact tests designated that impact strength increased significantly after 30 % elastomer content. Thermal analyses of the composites were done by using a DSC (Differential Scanning Calorimeter). Degree of crystallinity of ternary system decreased with increasing elastomer content, but melting points of the composites were not affected significantly. SEM micrographs showed that the adhesion between the matrix and fiber increased considerably with elastomer addition.

Keywords: Composites, Poly(ethylene terephthalate), Glass Fiber, Elastomer, Impact Modification, Mechanical Properties

ÖZ

POLİ(ETİLEN TEREFTALAT) BAZLI KOMPOZİTLERİN PROSESİ VE KARAKTERİZASYONU

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Polimerik kompozitler iki ya da daha fazla malzemeyi ayrı fazlar şeklinde içeren ve bu malzemelerden en az biri polimer olan kompozitlerdir. Herhangi bir polimeri cam, karbon ya da başka bir polimerle karıştırarak, polimerin istenilen özelliklerinin geliştirilmesi mümkündür.

Bu çalışmada matriks malzemesi olarak geri kazanılmış poli(etilen tereftalat) PET, güçlendirici olarak kısa cam elyaf (KCE) ve darbe dayanımını arttırıcı olarak elastomer kullanılarak üçlü kompozitler hazırlanmıştır. Şişe sınıfı geri kazanılmış PET, etilenin terpolimeri olan ve metil akrilat/glisidil metakrilat içeren bir elastomerle çift vidalı ekstrüderde karıştırılmış ve E tipi kısa cam fiber de yan besleyiciden ekstrüdere beslenmiştir. Çalışmada PET, ağırlıkça yüzdesi 10'dan 50'ye kadar olan elastomer ile karıştırılmıştır ve ağırlıkça yüzdesi 10'dan 40'a kadar olan KCE sisteme eklenmiştir. Ekstrüzyon sırasında ekstrüder proses parametreleri sabit tutulmuştur. Elde edilen kompozitler sonra baskılı kalıplama tekniğiyle karakterizasyon deneyleri için kalıplanmışlardır.

Üretilen kompozitlerin mekanik ve termal özellikleri ve morfolojileri karakterize edilmiştir. Kompozitlerin eriyik davranışları ve fiber boyu dağılımları da seçilen kompozitler için belirlenmiştir. Üçlü sistemlerdeki en yüksek çekme dayanımı değerleri ağırlıkça % 10 elastomer içeren kompozitlerde gözlenmiştir. Yüksek çekme ve eğilme modülü değerleri % 20 elastomer içeren kompozitlerde elde edilmiştir. Darbe dayanımı testleri, elastomer içeriği % 30'dan fazla olan kompozitlerde darbe dayanımının önemli ölçüde arttığını göstermiştir. Kompozitlerin termal analizleri DSC (Diferansiyel Taramalı Kalorimetre) ile yapılmıştır. Kompozitlerin kristallenme dereceleri artan elastomer miktarı ile azalmış, buna karşılık erime sıcaklıkları fazla etkilenmemiştir. SEM mikrografları fiber ile matriks arasındaki yapışmanın artan elastomer oranlarıyla belirgin bir şekilde arttığını göstermiştir.

Anahtar Kelimeler: Kompozitler, Poli(etilen tereftalat), Cam Fiber, Elastomer, Darbe Dayanımının Geliştirilmesi, Mekanik Özellikler

To Mum, and my sister Burçak...

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CHAPTER I

INTRODUCTION

Polymeric composites are any of the combinations or compositions that comprise two or more materials as separate phases, at least one of which is a polymer. By combining a polymer with another material, such as glass, carbon, or another polymer, it is often possible to obtain unique combinations or levels of properties. Typical examples of synthetic polymeric composites include glass, carbon, or polymer-fiber-reinforced thermoplastic or thermosetting resins, carbon-reinforced rubber, polymer blends, silica or mica-reinforced resins. Typically, the goal is to improve strength, stiffness, or toughness, or dimensional stability by embedding particles or fibers in a matrix or binding phase. A second goal is to use inexpensive, readily available fillers to extend a more expensive or scarce resin; this goal is increasingly important as petroleum supplies become costlier and less reliable [1].

Poly(ethylene terephthalate), PET is an important engineering thermoplastic which is widely used all around the world. The basic sources of raw materials for PET resin production are crude oil and natural gas. PET is a condensation polymer derived from terephthalic acid (TPA) or dimethyl terephthalate (DMT) and ethylene glycol (EG). The great acceptance of PET as a packaging material is due to its toughness, clarity, capability of being oriented and reasonable cost. Compared to glass, PET containers are lightweight and shatter-resistance. They provide an acceptable barrier and they are considered as the most recyclable plastics abroad.

Each year millions of tons of PET remain as scrap after being used in several areas. As a result of the governmental and environmental regulations, PET is being recycled. In order to get rid off reduction in mechanical and processing properties PET is mostly being reused again by either reinforcing or toughening. Sometimes both of them are applied and composites are prepared.

In this study, bottle grade recycled PET was blended with both an elastomer which is a terpolymer of ethylene/methyl acrylate/glycidyl methacrylate (E-MA-GMA) and short glass fiber (SGF). In order to obtain well mixing, a twin screw extruder was used for composite preparation.

Short glass fiber which is widely used for composite reinforcement forms an orientation in the composite and increases the mechanical properties, especially the tensile properties of the composites. It is preferred among the other fibers due to its high strength versus cost ratio.

Elastomer is defined as a macromolecular material which, at room temperature, is capable of recovering substantially in shape and size after removal of a stretching force. Crosslinking improves an elastomer’s ability to return to its original state after being distorted. They are widely used for impact modification purposes.

Chaudhari et al. [2] used an elastomer which is also a terpolymer of ethylene with the functional group glycidyl methacrylate in order to increase the impact properties of the recycled PET, and observed significant increase in impact properties.

The main objective of this study is to obtain ternary composites. These composites were prepared to obtain high impact strength recycled PET at room temperature without forsaking the tensile properties. In addition to this main objective, to improve thermal and morphological properties are the minor goals. For determination of the mechanical property improvement, binary composites, including glass fiber-recycled PET and binary blends including elastomer-recycled PET were also prepared for comparison.

Mechanical characterizations of the composites were performed by tensile, flexural and impact tests. The mechanical behavior of the reinforced and impact modified composites was evaluated in terms of impact strength, tensile properties (tensile strength, tensile modulus, elongation at break) and flexural properties (flexural strength, flexural modulus) at different short glass fiber and elastomer contents. Thermal characterizations were done by using a differential scanning calorimeter (DSC) and morphological characterizations were made by using scanning electron microscope (SEM). In addition to these, to determine the melt behavior of the composites, melt flow index measurements were also performed.

Lastly, the effects of elastomer type and mixing protocols in extrusion were studied to determine their effects on the final properties of the composites and in order to recommend the effects of these parameters for future studies.

CHAPTER II

BACKGROUND INFORMATION

2.1 Poly(ethylene terephthalate), PET

Poly(ethylene terephthalate), PET, is one of the most commercially used thermoplastic. PET is a linear condensation polymer that has been used in applications that have seen rapid growth especially as packaging material for carbonated beverages since it was introduced as a container resin. Prior to this surge in use, PET was used as food packaging film, including boil-in-bags for frozen vegetables, and most commonly for the production of fiber for clothing and other applications. The structure of PET is as follows [3]:

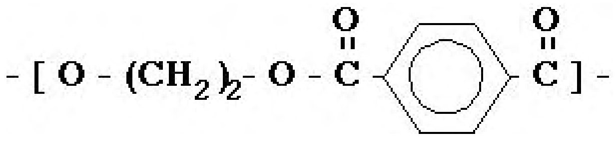


Figure 2.1 Chemical structure of PET

2.1.1 History of PET

The first laboratory samples of poly(ethylene terephthalate) in fiber form were developed by Calico Printers Association [4], a small English company, in 1941. Polyester research began in the United States after World War II. In the 1950s, this research was based on textiles such as DuPont's Dacron™ and ICI's Terylene™. In 1962, the first polyester tire cord was manufactured by Goodyear [4]. In 1977, PET was produced commercially for packaging applications such as film, sheet, coatings, and bottles - although oriented PET film was available in the 1950s. Since then due to the new improvements in mechanical and barrier properties, the consumption of the resin has grown rapidly, primarily for carbonated beverage bottles.

2.1.2 Chemistry of PET

PET is made industrially by two methods, the first step in each of which involves conversion of the TPA and DMT feed stock with ethylene glycol (EG) into bis (hydroxyethyl) terephthalate (BHET).

In the early stages, polymer technology was not developed to produce TPA with sufficient purity. In the early 1960s, pure TPA was produced directly from p-xylene with bromide-controlled oxidation.

DMT was made by esterification of terephthalic acid. However, a different process involving two oxidation and esterification stages is now used to produce most DMT.

The intermediate product, ethylene oxide is produced by oxidation of ethylene. Then ethylene glycol is obtained by reaction of ethylene oxide with water.

2.1.3 Formation of PET

PET is a step-growth (condensation) polymer derived from terephthalic acid (TPA) or dimethyl terephthalate (DMT) and ethylene glycol (EG) according to the following chemical reactions:

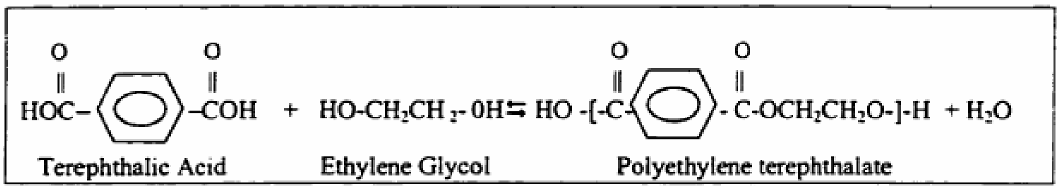


Figure 2.2 PET formation via acid route

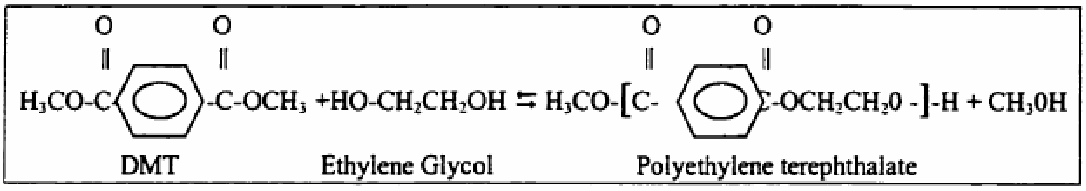


Figure 2.3 PET formation via ester interchange

In condensation polymerization, if the system is heated with antimony catalyst, a reversible reaction takes place between two polyfunctional molecules to produce one larger polyfunctional molecule, with the possible elimination of a small molecule such as water or methanol. The polycondensation rate is heavily dependent on the type and concentration of the catalyst. The reaction continues until almost all of one of the reagents is used up; an equilibrium is established which can be shifted at high temperatures by controlling the amounts of the reactants and products. “Copolyesters, which are produced commercially to reduce the crystallinity of PET, are made by replacing the TPA or EG portion with another dibasic acid or glycol or both. The step growth polymerization occurs in two steps: First, a low molecular weight precursor is formed (BHET), which is then transesterified to form a high molecular weight reactor grade resin.

To achieve very high molecular weights (I.V.: 0.72-0.84) and thus avoid thermal degradation in the melt, condensation is also performed in solid phase in a vacuum or under nitrogen. The molecular weights of the PET are adjusted to the intended application area” [5], which were given in Table 2.1.

Table 2.1 Application areas and molecular weights of PET [5]

PET Application	IV_{DCA} (dl/g)	MW Range
Fibers	0.57 – 0.65	38500 - 46000
Fibers, low pilling	0.39 – 0.51	23000 – 32000
Filaments, textile	0.65 – 0.68	46000 – 49000
Filaments, technical	0.65 – 1.00	46000 – 84000
Bottles	0.70 – 1.00	51000 – 84000
Films	0.59 – 0.69	41000 – 51000

2.1.4 Morphology of PET

PET is a linear molecule that exists either in an amorphous or a crystalline state. In the crystalline state, the molecules are highly organized and form crystallites, which are crystalline regions that extend no more than a few hundred angstrom units. The maximum crystallinity level that can be achieved is probably no more than 55 %. The crystallinity in the PET soft drink bottle is normally about 25 % [4]. PET produced by solid stating comes from the reactor in crystalline form. It is shipped to the fabricator in this form. Polymers in either amorphous or crystalline form can be uniaxially or biaxiallly oriented. In either case, orientation greatly increases the strength of PET; because strain induced orientation usually imparts some crystallinity.

As the crystalline state is the normal state for PET, the amorphous PET is produced deliberately. Amorphous PET is prepared by rapidly cooling the molten resin from a melt temperature of 260 °C to temperature below the glass transition of 73 °C. On the other hand, slow cooling of the molten resin will produce a crystalline polymer. A recycler of PET who produces pellets by extrusion will normally produce crystalline polymer. It is important to do so because pellets of crystalline PET are preferred by the processor, who normally dries the recycled PET before using it. Amorphous resin tends to soften and stick at elevated temperatures of drying, forming clumps and adhering to the walls of the drying unit.

The crystallization rate of PET is very important in processing. Crystallinity has a great effect on the product clarity and processability. However, if the size of the crystallite is small enough to minimize light scattering, clarity can be achieved in spite of the crystallinity of the polymer.

2.1.5 Properties of PET

The rapid growth of PET is due to the following properties:

- can be used as an amorphous or partially crystalline material,
- has good impact strength,
- can be made transparent or opaque as required,
- permits continuous service temperatures of around 180 °C (partially crystalline) and 60 °C (amorphous),
- is environment-friendly; it can be recycled or incinerated to form carbon dioxide and water, leaving virtually no residue,
- offers an excellent price/performance ratio.
- very good chemical resistance

Some properties of PET are given in Table 2.2.

Table 2.2 Some properties of PET [6]

Property	Value	Units
Specific Gravity	1.37 – 1.38	---
Crystalline Melting Point	250 – 255	°C
Vicat Softening Point	261	°C
Moisture absorption (in water)		
24 h at 23°C	0.02	%
2 h at 100°C	0.1	%
Tensile Strength (at yield)	71.5	MPa
(at break)	52.9	MPa
Flexural Strength	110.3	MPa
Flexural Modulus	2758	MPa
Izod Impact Strength	29 – 38	J/m
Elongation	70	%
Rockwell Hardness	120	M Scale

2.1.6 Processability

PET can be processed by different methods such as melt spinning, injection molding, stretch blow molding, flat-film extrusion, thermoforming, etc. The resulting products (e.g. fibers, films, injection-molded articles, bottles, and sheets) can be colored, adhesive bonded, welded, painted and laser marked.

2.1.7 Applications and Markets of PET

The fact that the mechanical properties of PET, especially its impact resistance, improved by biaxial drawing have contributed to the success that PET has experienced throughout the packaging sector. This trend is continuing and PET is also expected to expand its future market share. The Western European market is expected to experience PET growth rates of about 8 % annually during the next few years. In Europe, 500000 metric tons and 70000 metric tons of PET are consumed annually for drinking bottles and packaging films respectively. Polyester bottles have gained wide acceptance as soft drink containers for the following reasons:

- 93 % weight saving compared to glass,
- high barrier properties, especially for oxygen (O_2) and carbon dioxide (CO_2)
- excellent transparency and gloss,
- very good mechanical properties,
- shatter-resistance up to drop height of 2.5 m,
- shock-resistant and tough,
- very good chemical resistance,
- approved for food contact (FDA/ BGA),
- readily recyclable.

PET has also gained favor in other food packaging applications other than carbonated beverage containers. Syrups, oils, and mustard can now be found in PET bottles. Nonfood packaging items include those for cosmetics, toiletries, and household products. PET film is used for photographic film and magnetic tapes [7]. New developments have led to use of PET in manufacturing of beer and other hot fill applications [8]. Disposable PET containers are now being used in hospitals for wound drainage systems [9]. The bottles are extrusion blow molded, radiation sterilized, and they exert and maintain a constant starting vacuum of 600 mmHg to provide optimum suction for wound drainage. Foam of crystalline PET, known as Cell-PET, has been developed by Sekisui Kaseihin Kogyo Company, Japan [10]. This foam has high thermal resistance and has good potential to be used in packaging of foodstuffs. Glass fiber reinforced PET can also be used in electrical and electronic goods [11]. It can be used in appliances such as sandwich toasters, tabletop ovens, cooker components and electric irons. PET can also be used in electrical components such as power switches, light bulb bases, and sensor housings, as well as in specialized applications such as housings for measuring instruments.

2.2 Recycling of Plastics

2.2.1 Introduction

The recycling of homogeneous polymers is a relatively easy challenge only when their structure is preserved and no significant degradation took place both during the lifetime and during the processing operations. Indeed, the degradation phenomena, causing decrease of the molecular weight, formation of branching and of other chemical groups, etc., give rise to a remarkable worsening of all the physical properties. If the secondary materials obtained from recycled plastics had lower physical properties than the virgin plastics then they will be less valuable. The more relevant challenge in the recycling of plastics is then to avoid further degradation of the polymer structure during reprocessing operations and then a further worsening of the final material. This can be obtained by means of a correct choice of the processing machines and by adding stabilizers and other additives before each melt operation [12].

2.2.2 Recycling of Engineering Thermoplastics

Within the wide field of polymeric materials, engineering thermoplastics are characterized by a favorable combination of properties include remarkable mechanical properties, comparatively high thermal and hydrolytic resistance and, in many cases, outstanding resistance to chemical agents. These points make the plastics essential in many engineering applications such as automotive, household, electrical, electronic, communication and aerospace.

Recycling of plastics with different chemical natures, or of plastics containing contaminants, may greatly deteriorate the properties of the final material with respect to those of virgin one. Therefore, in case of engineering thermoplastics, as the properties have to be maintained at a high level, recycling requires a very careful separation to avoid the presence of even small amounts of any other component. Thus, upon reprocessing, the basic nature of the material is maintained, although the thermal-mechanical history changes [12].

Reprocessing requires that the scrap pieces be granulated. Thus, the polymeric material is subjected to at least two consecutive temperature-shearing cycles that may produce thermal, thermo oxidative or mechanical degradation. These degradative processes may affect the chemical structure and the molecular weight of the polymer to an extent. Also the number of processing cycles applied may affect the properties. The structural changes may lead to a deterioration of, among others, mechanical properties, which determine the applications of the recycled material [12].

2.2.3 PET Recycling

Plastics are a small but significant component of the waste stream. Plastics have become an integral part of our lives. The amount of plastics consumed annually has been grown steadily. Its low density, strength, user-friendly design and fabrication capabilities and low cost, are the drivers to such growth. Besides its wide use in packaging, automotive and industrial applications, they are extensively used in medical delivery systems, artificial implants and other healthcare applications, etc.

PET recycling represents one of the most successful and widespread examples of polymer recycling. In 1998, 10.4 x 10^4 tons of PET was recycled in Europe compared to 3.6 x 10^4 tons in 1995 and only 2.3 x 10^4 tons in 1993. The main driving force responsible for the increase in recycling of post consumer PET is its wide spread use, particularly, in the beverage industry which has made PET the main target for plastics recycling.

The main problem during material recycling is the segregation of polymers. A polymer after segregation is typically not completely pure. The presence of contaminants generates some problems such as cleavage of chains, an increase in carboxylic end groups, a reduction in molecular weight, a decrease in intrinsic viscosity (I.V.) leading to a decrease in mechanical properties of the material. The main problem in recycling of PET is the elimination of all impurities that may catalyze hydrolysis. The most common impurities enhancing hydrolysis are: polyvinyl chloride (PVC) [13], sodium hydroxide (NaOH) or alkaline detergent from labels on PET bottles. The hydrolysis of PET is an autocatalytic process because the end hydroxyl groups transform into carboxyl groups that catalytically accelerate further hydrolysis. Simply heating PET at elevated temperature in the absence of moisture can lead to the formation of carboxylic acid end groups, as shown in Figure 2.4 [4]:

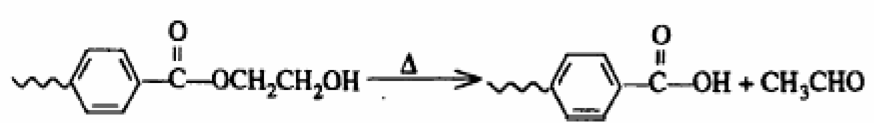


Figure 2.4 Formation of carboxylic end groups

This reaction converts a hydroxyl end group into a carboxylic acid end group that can catalyze hydrolysis. Taking this chemistry into account, the industry has recognized that extruding virgin PET that has been adequately dried (a moisture content of 0.005 %) still will cause a modest reduction of the molecular weight of the PET, as measured by the drop in intrinsic viscosity. Each time virgin PET is extruded the I.V. drops by 0.02 - 0.03 units.

The processing of recycled PET involves thermal and hydrolytic degradation of a polymer, which reduces the molecular weight, the intrinsic viscosity, and the mechanical properties of recycled materials. Degradative effects can be limited by using chain extenders. Chemical modification of recycled PET by diisocyanates leads to increase in the molecular weight from 30000 to 51000 g/mol, the intrinsic viscosity from 0.60 to 0.84 dL/g, and mechanical properties, particularly the elongation at break, from 5 to 300 % [14].

2.2.3.1 History of PET Recycling

The recycling of poly(ethylene terephthalate) soft drink bottles began after their introduction in 1977 because some states had laws requiring a deposit on all beverage containers. By 1989, the recycling rate had increased to 23 % up from only 10 % in 1982. In U.S. more than 90 % of the bottles were collected from deposit sites in 1989. Over the past decade, the technology for recycling PET soft drink bottles has been advancing rapidly. Though most commercial recycling systems depend on some flotation system to separate PET from the high-density polyethylene (HDPE) base-cup resin, alternative systems have been developed. One of the serious contaminants in PET recycling is the adhesive used to attach the base cup and the label to the PET bottle. Today, new technology has minimized this problem and has allowed the recycling industry to produce a very pure recycled PET [4]. According to a survey carried by NAPCOR the PET bottle industry continued its strong growth in 1997. ASG (Analytical Sciences Group) determined that 2.551 billion pounds of PET bottles and jars were available for recycling in 1997 in the U.S., which represents an almost 16 % increase from 1996. The additional new applications, particularly in the area of hot filled bottles and jars, are expected to lead this continued strong growth in 1998.

2.2.3.2 Effect of Contaminants on PET Recycling

“A major concern during reprocessing of PET is to remove all contaminants that can catalyze the hydrolysis of PET. Also, the reprocessor must avoid adding such cleaning agents as caustic soda in the wash step. These compounds are sometimes used to help removal of labels. Often, adhesive residues are trapped in the PET granules and remain there after washing. Since these adhesives darken when treated at PET extrusion temperatures, the recycled PET becomes discolored and hazy. During removal of labels, ionic or non-ionic surfactants are used to prevent the re-sticking of the PVA adhesive on to the flakes. If not cleaned properly, residual contaminants in recycled PET could be a risk to the public health, especially when intended to use for direct food contact applications" [4]. Also PVC content exceeding 50 ppm in the scrap PET makes it worthless for advanced applications such as film forming [15].

2.2.3.3 PET Recycling Techniques

2.2.3.3.1 Mechanical Recycling of PET

At the present time most recycled PET bottles are cleaned (washed), flaked and either used directly or blended with virgin polymer, before professing in a similar way to virgin polymer. Purity of the PET material is essential; mechanical recycling of PET is particularly sensitive to the presence of PVC. Very small quantities can cause material degradation and even damage equipment during reprocessing. The acceptable level of PVC is less than 0.25 %. Some of the mechanical recycling techniques commonly used are discussed below [4].

2.2.3.3.1.1 Flotation or Hydrocyclone Process

Hydrocyclone is a centrifuge device with a greater gravity force that simply accentuates the action of a sink-float tank. In this process PET and high density polyethylene (HDPE) are separated by differences in their density. In this process the system is fed with crushed, baled bottles with and without caps. If the bales consist of both green and colorless bottles, the bottles are color sorted by hand or by photo-cell (sensors). The dirty, sorted bottles are first reduced to 32-9.5 mm (0.125-0.375 in.) flake by being processed through a granulator. Labels and loose dirt are removed by blowing air at low pressure. The contaminated flake is then metered into an agitated washing tank along with a hot non-foaming detergent solution. All recyclers have their own detergent recipes, a preferred solids concentration in the slurry, and a preferred temperature and wash cycle. The use of caustic soda in the wash solution is not recommended because it facilitates the hydrolysis of PET chains that results in drop in intrinsic viscosity. The washing step removes the last traces of label material and disperses and sometimes dissolves the adhesives. The polymer flakes are thoroughly rinsed with fresh water to remove residual wash solution, label and other materials. Now cleaned, the crude flake or chip moves into hydro-cyclone that separates the heavy PET from light HDPE in water medium. HDPE floats in water while PET sinks. Ethylene vinyl acetate (EVA), if present from the cap liner, stays with the HDPE. The effectiveness of the hydrocyclone depends on the concentration of the solids and the speed of the centrifuge. The "heavy" and "light" product streams from the tank or the hydrocyclone are typically flushed once more with fresh water and processed first through spin dryers and then through hot air dryers. Then the metal impurities (if any) are removed by feeding the PET flakes into the multistage electrostatic separator. An interesting variation on the flotation or hydrocyclone process is the addition of a step that granulates or grinds the PET bottles cryogenically. Because adhesive contaminants are embrittled at cryogenic temperatures, whereas PET is not, adhesive contaminants in a cryogenic process become a fine powder. The fines are easily removed from the coarser PET flake by screening [4].

2.2.3.3.1.2 Water Bath / Hydrocyclone Process

This process developed by Reko, a division of DSM in Holland, operates either with PET bottles that have plastics caps or with cap-free bottles. In this process, bottle components are substantially separated before granulation. Color-sorted crushed bottles from the bale move continuously through a hot water bath (1 - 1.5 min.) that is at least 70 °C and close to

100 °C. At these temperatures, the PET bottles, which are blow-molded by a process that orients the PET, shrink. As a result, the labels and caps, which do not shrink, separate from the PET bottles. From the immersion tank, the separated components are deposited on a vibrating screen that removes the detached labels. After washing and rinsing, the PET flake in water medium moves through a hydrocyclone that removes any residual polyethylene and adhesives. Finally, the clean and dried recycled PET passes through a metal detector to ensure the absence of any traces of metal [4].

2.2.3.3.1.3 Solvent/Flotation Process

This system was developed by Dow Chemical. The process begins like the conventional flotation process, discussed before, but it is followed by a series of float/sink steps using chlorinated solvents. After the water-flotation step that separates the polyethylene and some labels from the PET flakes, the "heavies" move first through a float/sink step with 1,1,1-trichloroethane as the solvent and then through another float/sink step using a mixture of perchlomethylene and trichlomethane. The trichloroethane dissolves the adhesives and floats any remaining label materials. Finally, the solvents are removed and recovered in a closed distillation system and the adhesive free PET is dried.

2.2.3.3.2 Chemical Recycling of PET

Chemical recycling is also an established method for the recovery of process waste. However, equipment costs are high and require large turnovers to be economically viable. The condensation reaction of ethylene glycol and terephthalic acid shown in Figure 2.5, used for manufacture of PET, is a reversible reaction [4].

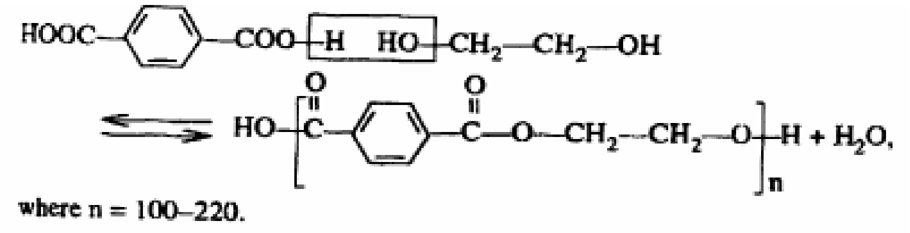


Figure 2.5 Condensation reaction of PET

The company that carries out the reversible reaction with glycols (glycolysis) instead of water can produce aromatic polyols that can be further treated with isocyanates or unsaturated dibasic acids to produce polyurethanes or unsaturated polyesters, respectively.

The selection of the most appropriate process is dependent upon the quality of the available feedstock and demand for intermediates formed. Glycolysis is unable to remove colors added to the PET feed-stream during the original formulation and, therefore require additional purification steps.

2.2.3.3.2.1 Hydrolysis/Methanolysis

Treating PET with water in excess at an elevated temperature of 150-250 °C in the presence of sodium acetate as catalyst produces terephthalic acid (TPA) and ethylene glycol (EG) in four hours. Catalysts for hydrolysis are either acids (such as sulfuric) or bases (such as ammonium hydroxide) [16]. An acid catalyst will promote the hydrolysis in 10-30 minutes at 60-95 °C. Alternatively, PET can be treated with an excess of methanol, as shown in Figure 2.6 to produce dimethyl terephthalate (DMT) and EG. A typical PET/methanol ratio is 1:4.

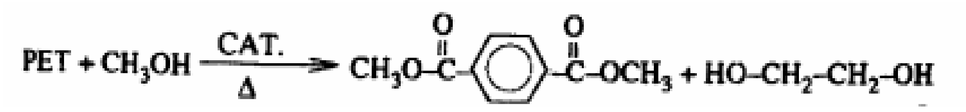


Figure 2.6 Methanolysis process

In a typical methanolysis process, molten PET is mixed with methanol and, if desired, a catalyst, and heated at 160-240 °C for less than an hour under a pressure of 20 - 70 atm. A 99 % yield of monomers is claimed [17].

2.2.3.3.2.2 Glycoloysis

If recycled PET is treated with excess glycol, a transesterification reaction takes place. The reduction of high molecular weight PET to short-chain fragments is achieved by heating the PET with a glycol such as propylene glycol (PG) in the presence of a catalyst. Typical catalysts are amines, alkoxides, or metal salts of acetic acid. Typically this glycolysis reaction takes place over an 8 hour period at 200 °C with a PG/PET ratio of 1.5:1 and major products are bis-hydroxyethyl terephthalate, bis-bydroxypropyl terephthalate, and mixed EG/PG terephthalate diesters, plus some free EG and PG. The reaction is carried out under continuous nitrogen purge to inhibit degradation of the resulting polyols. Under these reaction conditions, the resulting polyol has a number average molecular weight of 480 and a hydroxyl number of 480. If a higher molecular weight polyol were desired, the PG/PET ratio is lowered; i.e. less PG is used per mole of PET. Glycolysis reaction can also be done using glycerol, which produces a polyol with higher hydroxyl number, or with diethylene or dipropylene glycol (DEG).

Polyols made with DEG can produce polyurethanes with improved properties.

2.2.4 Applications of Recycled PET

Regrind PET can be used for reprocessing into cheap fiberfill for pillows and sleeping bags or used directly in filled and reinforced PET molding compounds. Another outlet for used PET is as a fuel source. According to Eastman, PET burns cleanly to produce carbon, oxygen, and water, and one pound of PET has the same heating value as one pound of soft coal. One of the uses of waste PET is its conversion to polyols for use in rigid or flexible urethane foams. Urethane foams made from recycled PET are relatively cheaper than those made from normal virgin polyols. A variety of clothing, including uniforms, working wear, T-shirts, polo-shirts, sweatshirts and using filament yarn, sweat shirts (jersey), wind-breakers (woven), bags (woven), tents (woven) and umbrellas (woven), are being manufactured from recycled PET bottles. Recycled PET is also used as the plastics clamshells for bakery and deli products. This clamshell is produced by thermoforming a 3-layer sheet in which the middle layer contains the recycled PET.

Previously recycled PET can not be used for food packaging due to the restriction of Food and Drug Association (FDA). But now after the development of new, advanced and sophisticated recycling processes, the FDA has started giving approval to recycled PET up to a certain level. This has opened new doors for the use of recycled PET. As one of the major users of plastic containers for food use, and as a leader in the beverage industry, The Coca-Cola Company has been involved in PET recycling from the start and was one of the first companies to receive a "no-objection" letter from U.S. FDA, allowing the use of recycled PET for food-contact application. Since then many different companies have taken an interest in developing some process for recycling PET so that it can be used in direct food contact packaging and have gained success [18]. The market of recycled PET for beer bottles is also igniting interest of various manufacturers [19]. Development in the field of reinforced recycled PET is also catching up. Glass/mineral filled PET is now being used as automotive grille opening retainers by Ford Motor Company, Mitsubishi Motors and Toyoda Gosei Co. Ltd. jointly are now molding car engine covers entirely from recycled PET soft drink bottles [20].

Extensive research investigated the use of resin based on recycled poly(ethylene terephthalate) plastics waste for the production of a high performance composite material, namely polyester concrete, for the construction industry. Resins using recycled PET offered the lower source cost of materials for forming good quality polyester concrete. Other applications include polyester resin for sail boats, shower units, and floor tiles, lumber, floor coverings, corrugated roofing, home insulation, industrial strapping, rope, non-food containers, light weight auto body parts, and machine housings.

2.3 Composite Materials

Composite materials are a material system composed of a mixture or combination of two or more macro constituents that differ in form or material composition and are essentially insoluble in each other. In principle, composites can be constructed of any combination of two or more materials–metallic, organic, or inorganic; but the constituent forms are more restricted. The matrix is the body constituent, serving to enclose the composite and give it bulk form. Major structural constituents are fibers, particles, laminae or layers, flakes, fillers, and matrices. They determine the internal structure of the composite. Usually, they are the additive phase. As the different constituents are combined, there is always a continuous region. It may simply be an interface, that is, the surface forming the common boundary of the constituents. An interface is in some ways analogous to the grain boundaries in monolithic materials. In some cases, however, the contiguous region is a distinct added phase, called an interphase. Examples are the coating on the glass fibers in reinforced plastics and the adhesive that bonds the layers of a laminate together. When such an interphase is present, there are two interfaces, one between the matrix and the interphase and one between the fiber and the interface. Interfaces are among the most important yet least understood components of a composite material. In particular, there is a lack of understanding of processes occurring at the atomic level of interfaces, and how these processes influence the global material behavior. There is a close relationship between processes that occur on the atomic, microscopic, and macroscopic levels. In fact, knowledge of the sequence of events occurring on these different levels is important in understanding the nature of interfacial phenomena. Interfaces in composites, often considered as surfaces, are in fact zones of compositional, structural, and property gradients, typically varying in width from a single atom layer to micrometers. Characterization of the mechanical properties of interfacial zones is necessary for understanding mechanical behavior [1].

Several classification systems for composites have been developed, including classification by basic material combinations, for example, metal-organic or metal-inorganic; bulk-form characteristics, such as matrix systems or laminates; distribution of the constituents, that is, continuous or discontinuous; and function, for example, electrical or structural.

2.3.1 Fiber-Matrix Composites

Fiber-matrix composites have two constituents and usually a bonding phase as well.

2.3.1.1 Fibers

The performance of a fiber-matrix composite depends on orientation, length, shape, and composition of the fibers; mechanical properties of the matrix; and integrity of the bond between fibers and matrix. Of these, orientation of the fibers is perhaps most important. Fiber orientation determines the mechanical strength of the composite and the direction of greatest strength. Fiber orientation can be one-dimensional, planar (two-dimensional), or three-dimensional. The one-dimensional type has maximum composite strength and modulus in the direction of the fiber axis. The planar type exhibits different strengths in each direction of fiber orientation; and the three-dimensional type is isotropic but has greatly decreased reinforcing values. The mechanical properties in any one direction are proportional to the amount of fiber by volume oriented in that direction. As fiber orientation becomes more random, the mechanical properties in any one direction become lower. Fiber length also impacts mechanical properties. Fibers in the matrix can be either continuous or short. Composites made from short fibers, if they could be properly oriented, could have substantially greater strengths than those made from continuous fibers. This is particularly true of whiskers, which have uniform high tensile strengths. Fiber length also has a bearing on the processibility of the composite. In general, continuous fibers are easier to handle but have more design limitations than short fibers.

2.3.1.2 Bonding

Fiber composites are able to withstand higher stresses than their individual constituents because the fibers and matrix interact, resulting in redistribution of the stresses. The ability of constituents to exchange stresses depends on the effectiveness of the coupling or bonding between them. Bonding can sometimes be achieved by direct contact of the two phases, but usually a specially treated fiber must be used to ensure a receptive adherent surface. This requirement has led to the development of fiber finishes, known as coupling agents. Both chemical and mechanical bonding interactions occur for coupling agents. Voids (air pockets) in the matrix are one cause of failure. A fiber passing through the void is not supported by resin. Under load, the fiber may buckle and transfer stress to the resin, which readily cracks. Another cause of early failure is weak or incomplete bonding. The fiber-matrix bond is often in a state of shear when the material is under load. When this bond is broken, the fiber separates from the matrix and leaves discontinuities that may cause failure. Coupling agents can be used to strengthen these bonds against shear forces.

2.3.2 Types of Composites

In many advanced composites the matrix is organic, but metal matrices are also used. Organic matrix material is lighter than metals, adhere better to the fibers, and offer more flexibility in shaping and forming. Ceramic matrix composites, carbon-carbon composites, and intermetallic matrix composites have applications where organic or metal matrix systems are unsuitable.

Epoxy resins have been used extensively as the matrix material. However, bismaleimide resins and polyimide resins have been developed to enhance in-service temperatures. Thermoplastic resins, polyetherketone, and polyphenylene sulfide are in limited use. The continuous reinforcing fibers for organic matrices are available in the forms of monofilaments, multifilament fiber bundles, unidirectional ribbons, roving (slightly twisted fiber), and single-layer and multilayer fabric mats. Frequently, the continuous reinforcing fibers and matrix resins are combined into a non final form known as a prepreg.

Metal-matrix composites are usually made with alloys of aluminum, magnesium, or titanium; and the reinforcement is typically a ceramic in the form of particulates, platelets, whiskers, or fibers, although other systems may be used. Metal-matrix composites are often classified as discontinuous or continuous, depending on the geometry of the reinforcement. Particulates, platelets, and whiskers are in the discontinuous category, while the continuous category is reserved for fibers and wires. The type of reinforcement is important in the selection of a metal-matrix composite, because it determines virtually every aspect of the product, including mechanical properties, cost, and processing method. The primary methods for processing of discontinuous metal-matrix composites are powder metallurgy, liquid metal infiltration, squeeze or pressure casting, and conventional casting; however, most of these methods do not result in finished parts. Therefore, most discontinuously reinforced metal-matrix composites require secondary processing, which includes conventional wrought metallurgy operations such as extrusion, forging, and rolling; standard and nonstandard machining operations; and joining techniques such as welding and brazing.

2.3.2.1 Ceramic-Matrix Composites

In general, ceramics are brittle engineering materials with limited reliability. Brittleness is connected with the structure and chemical bonding of the main constituents, and reliability is connected with the stochastic character of main phases and defect distribution within the polycrystalline ceramic body. In spite of the generally high strength, hardness, and chemical and shape stability of ceramics, these two negative properties disqualify their wider application in industry. Ceramic-matrix composites are designed as materials with higher fracture resistance (less brittleness), higher reliability, and in particular cases higher strength compared to monolithic ceramics.

These attributes are required for high technologies, especially in the aircraft, automotive, engineering, and energy industries.

Ceramic composites are materials with at least two constituents, the ceramic-matrix phase and reinforcing-toughening filaments. The filaments cover a wide range of dimensions, through micro-whiskers, to fibers that are several centimeters to a few meters long [21].

2.4 Polymeric Composites

Polymeric composites are any of the combinations or compositions that comprise two or more materials as separate phases, at least one of which is a polymer. By combining a polymer with another material, such as glass, carbon, or another polymer, it is often possible to obtain unique combinations or levels of properties. Typical examples of synthetic polymeric composites include glass, carbon, or polymer-fiber-reinforced thermoplastic or thermosetting resins, carbon-reinforced rubber, polymer blends, silica or mica-reinforced resins, and polymer-bonded or impregnated concrete or wood. It is also often useful to consider as composites such materials as coatings (pigment-binder combinations) and crystalline polymers (crystallites in a polymer matrix). Typical naturally occurring composites include wood (cellulosic fibers bonded with lignin) and bone (minerals bonded with collagen). On the other hand, polymeric compositions compounded with a plasticizer or very low proportions of pigments or processing aids are not ordinarily considered as composites [22].

Typically, the goal is to improve strength, stiffness, or toughness, or dimensional stability by embedding particles or fibers in a matrix or binding phase. A second goal is to use inexpensive, readily available fillers to extend a more expensive or scarce resin; this goal is increasingly important as petroleum supplies become costlier and less reliable. Still other applications include the use of some filler such as glass spheres to improve processability, the incorporation of dry-lubricant particles such as molybdenum sulfide to make a self-lubricating bearing, and the use of fillers to reduce permeability.

Emphasis on the development of polymeric composites has been stimulated by the need for greatly improved mechanical and environmental behavior, especially on strength-of stiffness-to-weight basis. Such composites are also often more efficient in their energy requirements for production than traditional materials. The high absolute and specific (per unit of weight) values of properties such as strength and stiffness have made composites ideal candidates for new applications in aircraft and boats, in passenger vehicles and farm equipment, and in machinery, tools, and appliances. Composites based on chemically resistant matrixes are used in chemical process equipment [23].

The behavior of composites depends upon the volume fractions of the phases, their shape, and on the nature of the constituents and their interfaces. With anisotropic phases, the orientation with respect to the direction of stressing or exposure to permeates is also important. In general, given an appropriate preferred direction, the greater the anisotropy the greater the effect on a given property, at least up to some point. Thus, all high-modulus reinforcements will stiffen a lower-modulus matrix, but fibers and platelets are more effective than spheres; a similar role of shape holds for the ability to reduce permeability at right angles to the anisotropic particles. Anisotropic high-modulus inclusions invariably increase strength if adhesion is good, but the effect is more complex with particulate fillers such as spheres. Rubbery inclusions lower the stiffness of a high-modulus matrix, but may enhance toughness by stimulating a combination of localized crazing and shear deformation [22].

Many fibers, for example, glass and carbon, are very stiff and strong. However, the maximum strength of these brittle materials cannot be realized in practical objects because of a high sensitivity to the inevitable small cracks and flaws which are ordinarily present. Most polymers are much less sensitive to such flaws, even though they are inherently less strong. More energy is needed to fracture a polymer than a ceramic or glass; a crack tends to grow much less readily in a polymer.

If, for example, a mass of a strong but flaw-sensitive ceramic or glass is divided into many parts, typically into a fiber, and embedded in a polymer matrix, a growing crack may break one fiber but its progress may be hindered by the matrix or diverted along the interfaces. Thus, even though the matrix contributes only insignificantly to the total strength, it permits a closer approach to the theoretical maximum strength of the glass. Similar considerations apply to short fibers and, with some qualifications, other forms of reinforcement.

The matrix has several other functions besides the dissipation of energy which would otherwise cause a catastrophic failure. It protects the fiber against damage by mechanical action, such as rubbing, or by environmental agents, such as water. It must also transfer an applied stress or force to the filaments so that they, being much stronger, can bear most of the load. In order to transfer the stress the matrix must adhere well to the fiber, though the optimum strength of the interfacial bond desired may vary depending on the application.

The strength of such a composite depends on the orientation of the fibers with respect to the applied force and on the nature of the stress (tensile or compressive). In the selection of materials and design for a composite, the ultimate application must be known. For example, strength of a composite based on longitudinally aligned fibers will be greatest in the direction of the fibers. Rupture under tension will require the pulling out of many fibers; this implies a fiber-matrix bond which can yield fairly readily, and in yielding increase the energy required for rupture. In compression, on the other hand, a stronger interfacial bond is needed to prevent buckling. Compromises in design are often necessary. Thus, at the expense of some strength, fibers are often crisscrossed in order to minimize the directionality of strength [23].

2.5 Polymer Blends

Polymer blend technology began in the plastics industry over fifty years ago. The ability to tailor the properties of two different polymers, in order to satisfy the property requirements of a particular application, is one of the main benefits of polymer blending. This approach is much cheaper than the start-up costs that would be necessary to produce a new polymer. Polyblends can be typically prepared by five techniques: melt solution, and latex blending, partial block or graft copolymerization, and synthesis of interpenetrating networks. Melt blending is a simple mechanical means of creating a homogeneous mixture of polymers. It could be performed on twin or single screw extruder, two-roll mill, or in an intensive mixer. In this study a twin screw was utilized.

The degree of mixing, temperature, and shear rate can be controlled on the twin screw extruder. The shear required to mix the polymers, without degrading them, can be tailored by programming the screw profile. Adjusting the screw speed can also alter shear. Different heating zones can control temperature of the polymer throughout the extruder barrel length.

The major advantage of melt blending is the absence of any solvents that might be required in other methods of polyblending. The major disadvantages are that mixing may be incomplete due to the kinetics involved in mixing large polymer molecules. The factors like temperature, shear, and time involved in the melt process can bring about degradation of the polymer. In blending reactive polymer system, these conditions could even cause premature crosslinking in thermoset materials. Solution blending eliminates concern of temperature and shear inherent in melt mixing. In this method, the two polymers are dissolved separately in the same solvent, after which, the two polymers solvent solutions are mixed. This is the preferred method in the coating industry. Drawbacks to solution blending include the exclusion of polymers that do not dissolve in the same solvent Problems with the solvent, including removal and toxicity, are also a concern [23].

The polymer morphology plays an important role in the behavior of polymer blends and alloys. Many studies on the miscibility of high performance polymer blends are being carried out because the miscibility is closely related to the physical properties of the blends. The miscibility behavior of polymer blends is greatly dependent on the method of blend preparation. For polymer blends with weak interfacial strength, various problems may arise which ultimately affect the performance of the article. Thermal analysis of polymer blends has shown that a miscible polymer blend will exhibit a single glass transition temperature (T_g) between the T_g's of the pure components, while for partially miscible systems the two T_g's approach each other but do not become identical. T_g of the polymer or polymer blends can be obtained by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), dielectric T_g measurement, and nuclear magnetic resonance (NMR).

The most important material properties, in commercial polyblending, are the rigidity and impact resistance of some plastics and the flexibility and strength of elastomers. Impact resistant rigid thermoplastics have experienced the greatest commercial success in the application of polyblending. Typically, a rubbery material is dispersed in a rigid thermoplastic. On impact, the rubber particles basically act as shock absorbers and stop the propagation of cracks through the rigid thermoplastic, through a variety of suggested mechanisms.

Flammability is another important thermal property aspect of polymer blends. The flame retardency of one polymer can be improved with the addition of a flame resistant polymer. Polyblending has important effects on the clarity of the blends. In most cases, two transparent materials blended together will become translucent or opaque. This is caused by difference in refractive indexes of the two polymers. As light passes through the blend, it crosses the interfaces between the two materials many times, and is repeatedly scattered, causing its opaque appearance. There are remedies to this condition. The particle size of the dispersed phase can be reduced to a size smaller than the wavelength of visible light. Another approach is to modify the refractive indexes of the material through copolymerization, until they match, since a polyblend of two transparent materials, with the same refractive index, will also be transparent. The clarity of some blends can also sometimes be improved by blending the copolymer of one polymer used.

Polymer blending can improve some chemical properties such as environmental stress cracking.

2.6 Plastics Reinforcement

Reinforced plastic can be defined as a plastic with strength properties greatly superior to those of the base resin, resulting from the presence of reinforcements imbedded in the composition. Plastics reinforcement is usually done by fibers and three types of fibers dominate the reinforcement market and all three share some basic characteristics. They are all very strong, very stiff, and can be made in continuous lengths. These three fibers are glass fiber, carbon or graphite fibers, and organic fibers [24].

The choice of which fiber will be used in a particular application depends largely on cost and performance. Glass fiber is the least expensive fiber, carbon fibers are the stiffest of the three major reinforcements and aramid fibers are the toughest. Some applications combine fiber types so that properties of one type enhance the properties of another. For instance, aramid fibers are excellent in tension, but poor in compression, whereas glass fibers are poor in tension but excellent in compression.

2.6.1 Mechanisms of Fiber Reinforcement

Figure 2.7 illustrates the examples of different reinforcement styles in the fiber content, type, length, orientation and hybridization. Randomly oriented chopped fiber based materials are generally at the lower property end. Continuous unidirectionaly fiber composites are the "high performance" materials. Short fibers are generally used for components that carry light loads or secondary structural applications. Continuous fibers are used in primary structural applications. Maximum properties can be achieved if all fibers are aligned in the fiber axis direction. Orthoscopic properties can be obtained by using alternating layers between 0 ^{o} and 90 ^{o}. Laminates can be made which are stacks of thin layers of fibers and matrix material. Generally, the fiber axis is in different directions for each layer of fibers used which helps in producing orthoscopic properties. Some of the new trends are to make 3-D weaves and braids are some of the newer techniques being used in the formation of fiber based composites [21].

Composites reinforced primarily with discontinuous fibers have lower mechanical properties than those with continuous fibers. This is because all of the loads in discontinuous fiber composites must be carried by the matrix in shear from fiber length to fiber length. Also, the volume of fiber in these materials is generally lower than in typical continuous fiber composites.

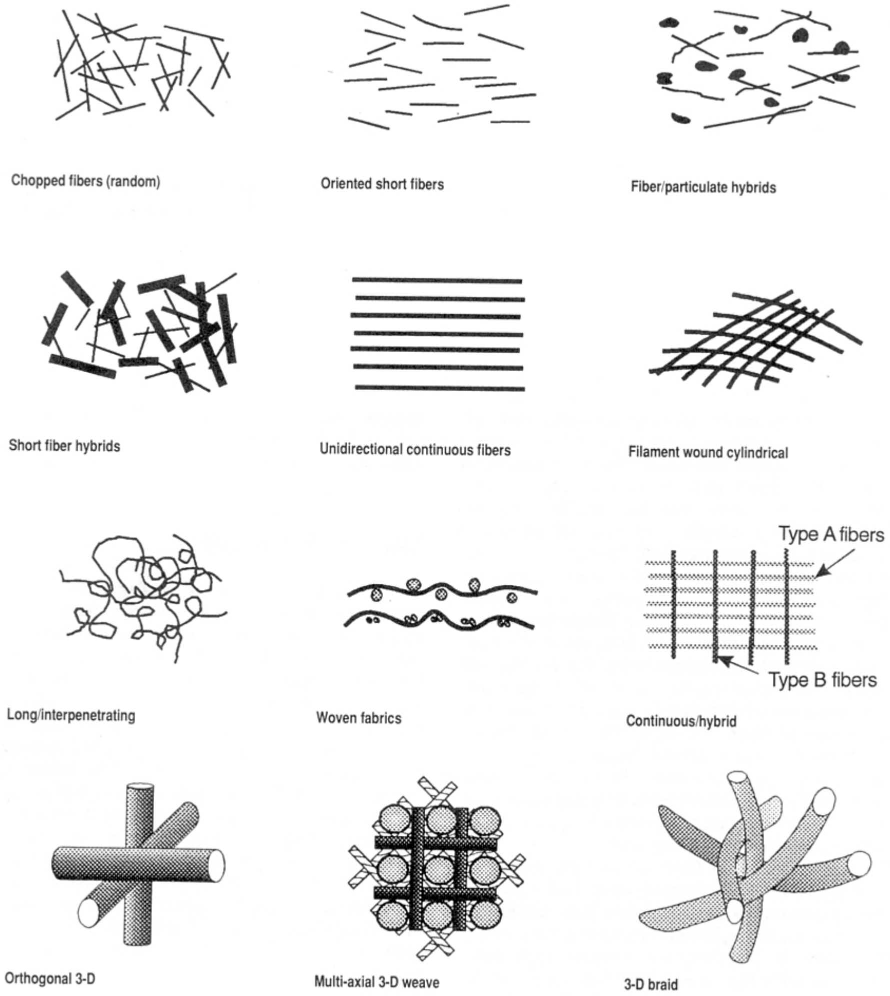


Figure 2.7 Examples of reinforcement styles, combinations, orientations and configurations of fibers in composites [21]

2.6.2 Glass Fiber

Glass fiber is made by spinning molten glass in much the same way that a synthetic fiber is spun from a melt. The thin strands of glass fiber are cooled and joined into bundles of fibers called tows. By including certain chemicals and using some special processing techniques, different types of glass fiber can be made. Glass fiber that has improved electrical resistance is called E-glass, glass fiber with improved chemical resistance is called C-glass, and glass fiber with high strength is called S-glass. Some advanced composites use S-glass to achieve special mechanical properties, but the most commonly used glass fiber for composites is E-glass, as it is the least expensive type [24].

After the glass fiber is formed, it is often treated with a chemical to give improved abrasion resistance to the fibers. Materials that are added to coat the fibers are called sizings or sizes.

Compatibility between the glass fiber and the resin is very important in achieving the optimum properties in composite. If the resin does not bond well to the reinforcement, the fiber can slip inside the composite when a load is placed on it. This slippage will decrease the stiffness and strength of the composite. To assist in improving the bond between the fiber and the matrix, the fibers can be coated with chemical agents called coupling agents. These coupling agents are molecules that have one end chemically similar to the resin and the other end chemically like the glass. The glass like end bonds to the glass fiber and then, when the resin is added to make the composite, the resin-similar end bonds with the resin, thus coupling the resin and glass fiber together.

A comparison of glass fiber with respect to different reinforcements is given in Table 2.3.

Table 2.3 Comparison of reinforcement fibers [24]

	Glass	Aramid	Carbon
Modulus (GPa)	72	117	227
Cost ($/kg)	2.20	35.00	22.00

2.6.2.1 Aspect Ratio of Fibers

Aspect ratio of fibers (length/diameter) is the other factor influenced by process conditions. During the extrusion and injection molding, shear stress exerted by the screw or ram will break the fibers and result finally in a fiber length distribution with an asymmetric character with a tail at long fiber lengths. The number average fiber length is defined as;

$$L_n = \frac{\sum N_i L_i}{\sum N_i} \qquad (2.1)$$

where N_i is the number of fibers of lengths L_i.

L_n is an indicator of the occurrence of short fibers [25]. The improvement in mechanical properties of fiber filled polymer is due to ability of withstanding a higher proportion of the mechanical load than the matrix it replaces. Fibrous filler is required in order to provide sufficient transfer of mechanical load from the matrix to the reinforcement. Such transference can only occur if the fiber length exceeds the critical length. Tensile loads acting on the fibers are zero at the ends and gradually increase to a plateau in the central portion of the fibers. So, the parts of the fibers near the ends carries less load then middle section. The sum of the length of the fiber on each end required for the tensile load to reach its plateu or maximum value is often called critical length. In other words, a fiber must have a length of at least critical length to achieve maximum stress in the fiber [26].

Fibers that are shorter than critical length will pull out the matrix under tensile load. For such a case, full load transfer is not realized. At the critical length both the fiber and matrix will fracture along the same failure plane. Additional increase in fiber length will not increase the strength of the composite, since the failure will be the same as that experienced at the critical length [27].

2.7 Impact Modification of Polymers

As mentioned before, PET has been widely used as engineering thermoplastic for packaging, electronics, and other applications. When blended with other polymers it offers an attractive balance of mechanical and barrier properties. In spite of these desirable properties of PET, the applications of these engineering plastics are quite limited because of its inherent notch-sensitivity in the fracture mode. A great deal of research is being conducted in an attempt to improve the impact toughness of PET. This can be achieved by blending of PET with an elastomer and using other high impact resistance polymers to modify its impact properties.

2.7.1 Theory of Impact Modification by Elastomers

The theory for the two-phase character of impact modified blends was first suggested by Buchdahl and Nielsen on the basis of dynamic mechanical properties of rubber-modified polystyrene obtained using the torsion pendulum [28]. The improvement in toughness is best understood by considering the nature of crack propagation during mechanical failure of rigid plastics. It is generally accepted that impact stresses create crazes (microscopic cracks) on the surface of the rigid polymer. Upon continued application of the stress, these micro-cracks develop into large rapidly moving cracks and brittle failure occurs. Under high stress, failure begins at any flaw or inhomogeneity where the stress may concentrate. Sharp comers, notches and voids acts as stress concentrators. Rigid plastics cannot respond to high speed impact and, thus, the stress concentrates at a single point and tears it apart in a single direction as shown in Figure 2.8. As the crack propagates through the rigid matrix, all of the energy remains concentrated at the apex of the growing crack, and continues the propagation rapidly. In a pure homogeneous rigid material, such crack propagation can proceed rapidly through the specimen, causing brittle failure.

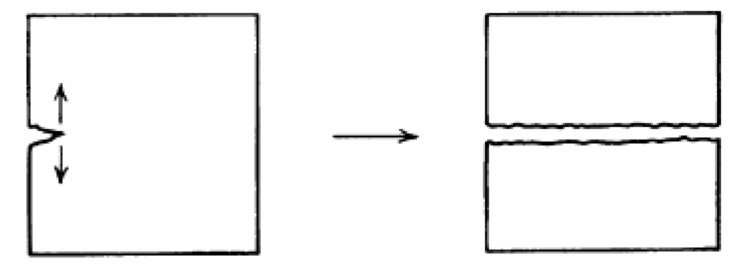


Figure 2.8 Fracture in rigid thermoplastics (brittle fracture) [3]

In toughened thermoplastics or a rubber modified thermoplastic an increase in energy is required to keep these cracks moving. It has been proposed that this is accomplished by converting high unidirectional impact stresses into smaller, harmless multi-directional stresses. Semi-compatible blends contain tiny soft or even rubber particles dispersed throughout the rigid plastic matrix. Many theories have been proposed to explain the improvement in the impact strength of a glassy polymer by addition of a rubber, and they are briefly explained below.

(a) A growing crack travels rapidly through the glassy polymer matrix until it reaches the rubbery domain. The rubber particle deforms rapidly without breaking and recovers elastically when the shock wave has passed. Much of the mechanical energy is utilized for this deformation and elastic recovery of the rubber particles, which slows and ultimately stops the crack propagation.

(b) When the growing crack comes across the rubber particle in brittle plastics, the rubber ligaments stretch across the widening crack. This puts the rubber in tension, which retards or stops the growth of the crack. This is represented in Figure 2.9;

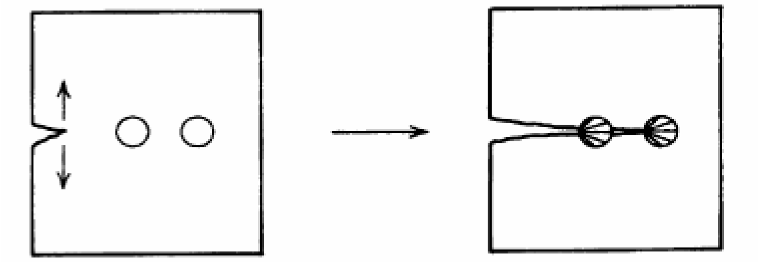


Figure 2.9 Fracture in elastomer toughened thermoplastics [3]

(c) The impact energy causing the growth of the crack is concentrated at the tip of the crack. When the crack reaches the rubber particle, the energy is dispersed throughout the particle. When this impact wave comes out of the rubbery particle, it is not concentrated at a point and the energy is insufficient to grow a new crack.

(d) When the crack reaches a rubbery particle some of the mechanical energy that propagates the crack is dissipated as heat and friction. This hysteresis wastes much of the original energy and does not leave enough energy for crack propagation.

(e) When the growing crack reaches the rubber particle, the particle nucleates the formation of many tiny craze cracks, which produces a large free surface that absorbs the mechanical energy as the potential surface energy. This is also a form of hysteresis in which the energy for crack propagation is dissipated.

(f) The hydrostatic tension lowers the glass transition temperature (T_g) of the rubber particle so that the rubber particle in the blend is softer than in a stress free state. It can be assumed that the thermal requirement to reach the T_g of the matrix is lowered due to the mechanical strain. The heat that has been generated due to friction and dissipation of the mechanical energy when the crack reaches a rubbery particle is enough to cause a yield in the entire matrix.

For improvement in impact resistance of glassy and brittle polymers such as PET, the following points are very crucial [29]:

- Uniform distribution of rubbery particles throughout the matrix
- Uniform size distribution of the rubbery domains
- Adhesion at the interlace of the rubbery domains and matrix

Addition of the rubber alone may not give the desired improvement in the impact resistance. It might be essential to have some type of primary or secondary bonding adhesion at the interface. Compatibilizers are sometimes used to functionalize the rubber or the PET or both to provide the required bonding. The processing methods and conditions as well as the type of rubber and compatibilizer generally control the size distribution of the rubbery domains and their dispersion throughout the matrix. An alternate approach to impact modification of condensation polymers such as PET involves incorporation of reactive functional groups into the elastomer. The in situ graft copolymer formed by reaction with the thermoplastic matrix reduces interfacial tension to improve dispersion during processing, and improves adhesion of the rubber to the thermoplastic in the solid state.

Another way to improve the impact resistance of the polymer is to create core shell structures. This technique increases the impact resistance and at the same time maintains the transparency of the polymer. Polymerizing the hard shell onto a soft rubber core forms the core shell structure. This structure provides excellent impact resistance properties, due to the soft rubber core, without adversely affecting the rigidity of the matrix, due to the hard outer shell. Moreover, the core-shell structure obtained by emulsion copolymerization offers the possibility of creating a defined particle size. Selection of appropriate monomers makes it possible to match the refractive index of the resin, resulting in tough, transparent polyester blends. Rubber such as acrylic and butadiene/styrene can be used as core material.

2.7.2 Impact Modification of PET

Tanrattanakul et. al. [30] reported that toughened poly(ethylene terephthalate) was obtained by blending with 1-5 % by weight of a tri-block copolymer with styrene end blocks and a functionalized ethylene mid-block. The mid-block was grafted by 2 wt. % maleic anhydride. Blending resulted in the formation of graft copolymer by reaction of hydroxyl end group of PET with maleic anhydride. It was found that as little as 1 % maleic anhydride grafted SEBS in PET increased the fracture strain by more than ten times. In the melt, the graft copolymer acted as an emulsifier to decrease the interfacial tension and reduce the tendency of dispersed interfacial tension and also reduced the tendency of dispersed particles to coalesce. In the solid state, the graft copolymer promoted adhesion between the phases in the blend and facilitated cavitations in a triaxial stress state. In addition, the dispersed particles acted as nucleating agent to enhance crystallization during yielding.

Jin-Gyu Park et. al. [31] claimed that when ethylene propylene diene elastomer (EPDM), grafted with an isocyanate-containing monomer was blended with PET, the impact resistance increased. Isocyanate containing monomer was incorporated onto the EPDM backbone through a solution graft reaction. When PET was blended with isocyanate-containing monomer-grafted EPDM (EPDM-g-HI), the morphologies of dispersed phases showed considerable differences in the aspects of particle size and interfacial adhesion compared with those of PET/EPDM blend. Dispersed particle sizes of the PET/EPDM-g-HI blends were finer than those of the PET/EPDM blends, and the PET/EPDM-g-HI blends showed homogeneous dispersions and even partial adhesion between the dispersed and matrix phases. Thermal analysis showed the PET phase in PET/EPDM-g-HI was somewhat amorphous compared with that in PET/EPDM blend. The improved compatibility of PET and EPDM, through functionalization of EPDM with the isocyanate moiety resulted in increase in complex viscosity, storage modulus and impact resistance. The key to improving compatibility and, thus, the properties of PET and EPDM blends, was the formation of in situ graft PET-EPDM copolymer through the chemical reaction between the isocyanate group of EPDM-g-HI and hydroxyl or carboxyl end groups of PET.

Apart from impact modification by blending with elastomer, the current study also concentrates on the aspect of reinforcing recycled bottle grade PET with short glass fiber.

2.8 Processing of Recycled PET Composites / Blends

During the studies of this thesis, for the preparation of composites/blends a twin screw extruder was used, so mainly will be focused on processing of the composites by extrusion.

2.8.1 Processing Techniques

2.8.1.1 Extrusion

The word extrusion comes from the Greek roots that mean to “push out”. This phrase correctly describes the extrusion process, which is, in essence, a pump that supplies a continuous stream of material to a shaping tool or to some other subsequent shaping process [24].

In addition to the shaping of parts by the extrusion process, extrusion is the most efficient and widely used process for melting plastic resin as part of the process of adding or mixing fillers, colorants, and other additives into the molten plastics. Extrusion can be used to shape the part directly after this mixing or an extruder can be used as the melting device that is coupled with other shaping processes.

A schematic and a cross-section view of the extrusion process are given in Figures 2.10 and 2.11.

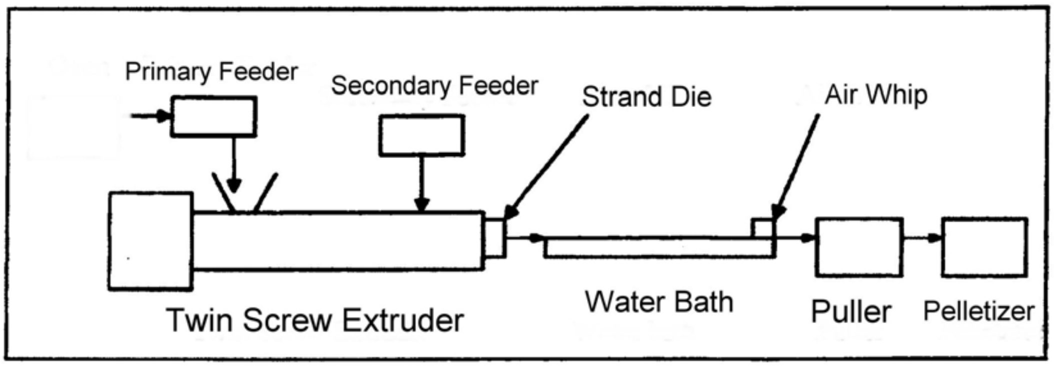


Figure 2.10 Schematic drawing of extrusion process

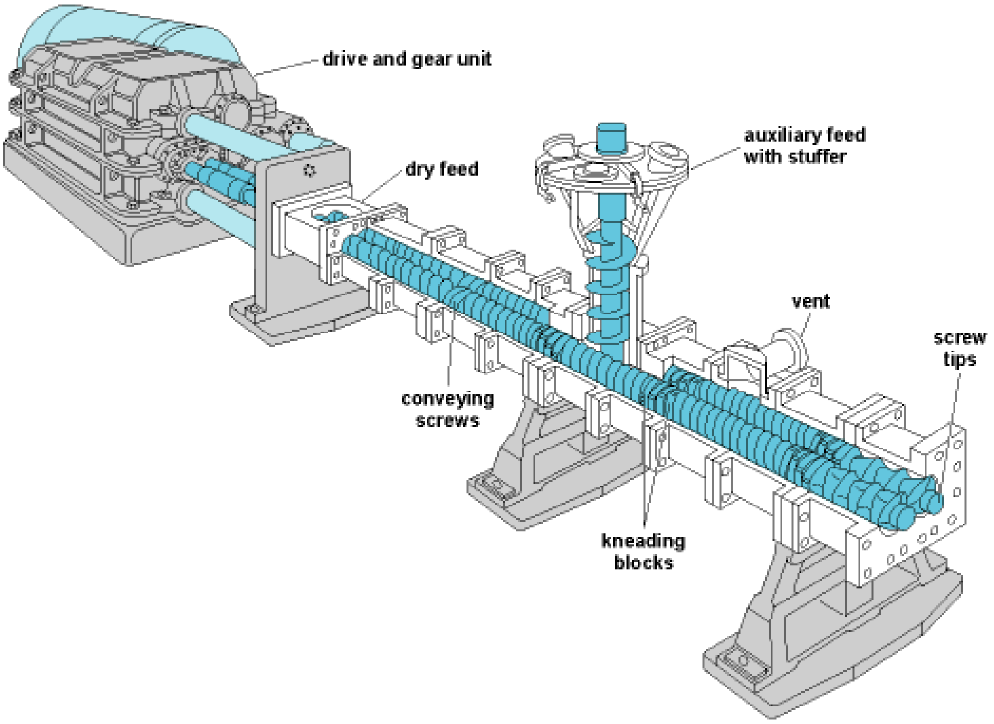


Figure 2.11 Cross-section view of extrusion process [23]

In normal plastics extrusion, plastics granules or pellets and any other materials to be mixed with them are fed into a hopper attached to the extrusion machine. From the hopper the materials falls through a hole in the top of the extruder onto the extrusion screw. This screw, that turns inside the extruder barrel, conveys the plastic forward into a heated region of the barrel where the combination of external heating and heating from friction melts the plastic. The screw moves the molten plastic until it exists through a hole in the end of the extruder barrel to which a die has been attached. The die imparts a shape to the molten plastic stream which is immediately cooled by a water bath. The output of the extruder is a continuous part. Auxiliary equipment is used to pull the part away from the extruder at the proper rate. Also another equipment cuts the part to the proper length [24].

During the extrusion process, volatiles such as solvents, water, or trapped air can easily be removed. The normal form of the product from extrusion process is thin rods that are chopped into the pellets. In addition to the long, thin rods that are chopped into pellets, other common extruded shapes include; pipe, sheets, fibers, coatings on wire and cable, coatings on paper, etc.

Thermoplastics are the most common plastics that are extruded. However, some thermosets can also be extruded, provided the temperature of the extruder is kept below the temperature that initiates the cure.

Detailed comparisons between the various processes used for forming plastic parts are difficult because of the different types of products and uses that are associated with each process. However, some broad comparisons can be made that point out basic advantages and disadvantages of extrusion versus the other processes as shown in Table 2.4.

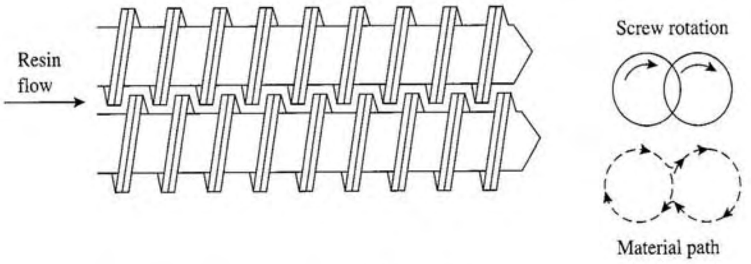
Table 2.4 Comparison of extrusion to other processing techniques [24]

Advantages	Disadvantages
Continuous High production volumes Low cost per pound Efficient melting Many types of raw materials Good mixing	Limited complexity of parts Uniform cross-sectional shapes only

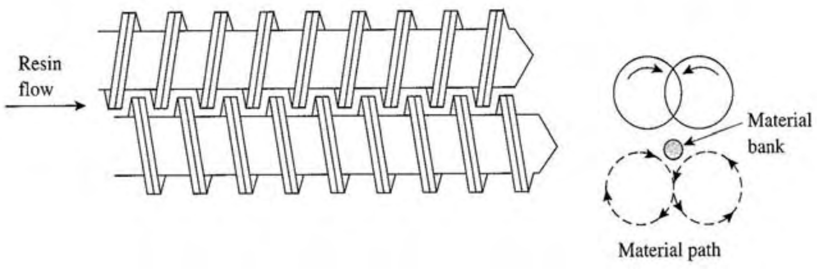
2.8.1.2 Twin Screw Extrusion

Twin-screw extruders have been mentioned as a type of extrusion that is valuable with certain resins, especially those that are sensitive to heat such as PVC. The use of twin screws, which operate side by side in tandem, requires different linkages and barrels. The screws in twin-screw extruders intermesh so that the relative motion of the flight of one screw inside the channel of the other acts as a paddle that pushes the material from screw to screw and from flight to flight. These extruders have a more positive pumping action than single-screw extruders and can therefore be used more effectively in high-output situations. This feature of twin-screw machines has led to their use in some applications which volume is critically important even though the resin may not be particularly heat sensitive [24].

Two different patterns for intermeshing twin-screw extruders are possible. In one pattern the screws rotate in the same direction, that is, both turn clockwise or both turn counterclockwise. This pattern is called corotating. In the other intermeshing pattern the screws rotate counter to each other, that is, one rotates clockwise and the other counterclockwise. This pattern is called counterrotating. Figure 2.12 shows different design patterns of a twin screw extruder.



(a) Corotating



(b) Counterrotating

Figure 2.12 Twin-screw extruder design patterns [24]

In the corotating screws system the material is passed from one screw to another and follows a path over and under the screws. The material moves alternately from the top of one screw to the top of the other, and then around the outside of second screw until it is on the bottom of the second screw, after which it then moves to the bottom of the first screw and then around the outside of that screw until it reaches the top again, but at a point farther along the screw length. This gives high contact with the extruder barrel, which improves the efficiency of the thermal heating. The path also ensures that most of the resin will be subjected to the same amount of shear as it passes between the screws and the barrel. Mixing is better in corotating systems than in either counterrotating or single-screw extruders.

In a counterrotating screws system the material is brought to the junction of the two screws and builds up in what is called a material bank on the top of the junction. This build up of material is conveyed along the length of the screw by the screw flights. As the material passes between the screws, high shear is created, but shear elsewhere is very low. Only a small amount of material passes between the screws. Therefore, total shear is lower than in single-screw extruders and in corotating twin-screw extruders. Most of the material in the bank along the junction of the screws is simply carried toward the end of the extruder. Hence, pumping is more efficient in counterrotating screw systems than in corotating systems [24].

2.8.2 Molding Techniques

2.8.2.1 Compression Molding

Compression molding was developed in 1909 by Leo Bakeland to produce radio cabinets [32]. Compression molding, also called matched die molding, is a molding process used almost exclusively for molding thermoset materials. When thermoplastics are concerned, these molding methods are usually called by separate names such as cold forming, sintering, or ram extrusion in addition to compression molding.

The principles of compression molding are quite simple. A charge of thermosetting resin is placed in the cavity of a matched mold that is in the open position. The mold is closed by bringing the male and female halves together, and pressure is exerted to squeeze the resin so that it is uniformly fills the mold cavity. While under pressure, the material is heated, which causes it to crosslink and to harden. When the material is hard, the mold is opened and the part is removed. Figure 2.13 represents the schematic drawing of a compression molding machine.

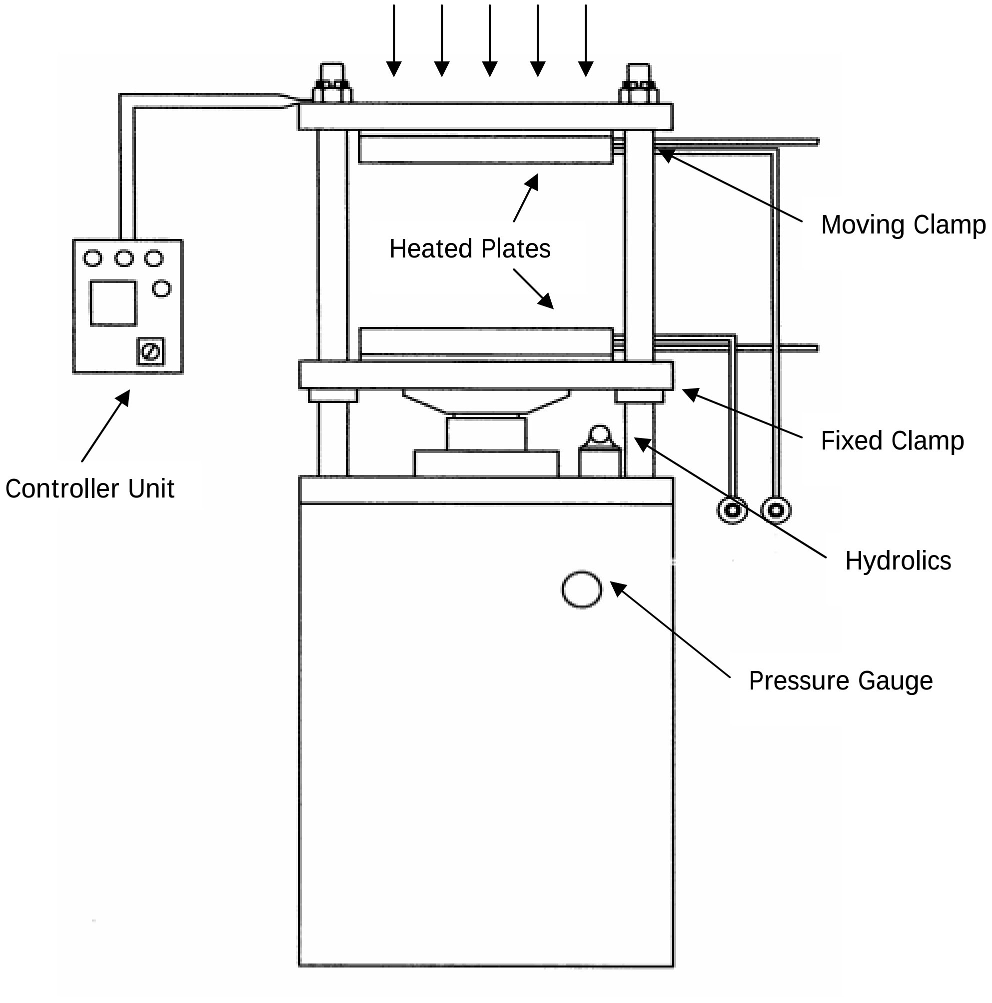


Figure 2.13 Schematic drawing of a compression molding machine

Compression molds are machined from steel. Their cavities are designed to be fully positive, semi-positive, landed positive or flash molds. The fully positive mold requires that the exact amount of material be placed in the mold. The fully positive mold does not allow excess material to flow out between the parting lines. Semi-positive molds allow for flash (material that flows out of the mold at the parting line) of excess materials just prior to the final closing of the mold. Landed positive molds allow for flashing in a prescribed area which forms a land or tab which can be removed and subsequently machine polished after molding. Flash molding allow for the elimination of excess materials during the final moments of the compression cycle. Products are more easily produced from flash mold since they do not require the exact amount of material, but they must be machined and polished in post molding operations.

This process is not one that is easily adapted to high volume production. A comparison between compression molding and injection molding processes is given in Table 2.5

Table 2.5 Comparison of Compression Molding and Injection Molding [24]

Property	Compression Molding	Injection Molding
Material	thermoset	thermoplastic
Mold heating	yes	no
Typical cycle	minutes	seconds
Recycle parts	no	yes
Mold open/close	open	closed
Types of parts	discrete	discrete
Part complexity	simple	complex
Hollow areas	difficult	easy with cores
Inserts	moderate	moderate to difficult
Undercuts	no	yes with slides
Part size	can be very large	size is limited
Flash	yes	no
Resin viscosity	moderate to high	typically low
Reinforcements	yes, can be long	some, cannot be long

2.8.2.2 Injection Molding

In contrast to the extrusion process, that makes continuous parts of constant cross section, injection molding makes discrete parts that can have complex and variable cross sections as well as a range of surface textures and characteristics. Almost all thermoplastics and some thermosets can be injection molded, thus adding to the flexibility of the process. Another important reason for the popularity of the injection molding is that parts are highly repeatable and the process is highly automatable. For some complex parts, injection molding is the only practical manufacturing process.

The difficulties of injection molding are the high cost of the machines and molds, the relatively high amount of process residue that must be reprocessed, the high level of competition because of the large number of molders capable of using the process, and the need for development and proper use of automated feedback and control systems [24].

The injection molding process is conceptually simple. In the process a plastic is melted and then forced into the cavity of a closed mold which gives shape to the plastic. After sufficient time for the plastic part to solidify, the mold opens and the part is removed.

2.9 Characterization of Recycled PET Composites/Blends

In the characterization part of this study, mechanical tests, fiber length distribution, scanning electron microscopy, differential scanning calorimetry, and melt flow index measurements were performed. Detailed explanation of each method will be given further:

2.9.1 Mechanical Tests

2.9.1.1 Tensile Properties

During tensile tests, a specimen is deformed, usually to fracture, with a gradually increasing tensile load that is applied unaxially along the long axis of a specimen.

The tensile test machine is developed to elongate the specimen at a constant rate, and to continuously and simultaneously measure the instantaneous applied load (with a load cell) and the resulting elongations.

The output of the tensile test is recorded on a strip chart as load or force versus elongation. Load and elongation are normalized to the respective parameters of engineering stress or engineering strain.

Engineering stress, σ is defined by the following relationship:

$$\sigma = \frac{F}{A_0} \qquad (2.2)$$

where F is the instantaneous load applied perpendicular to the specimen cross-section, and A_0 is the original cross-sectional area before any load is applied.

Engineering strain, ε is defined according to:

$$\varepsilon = \frac{L_i - L_0}{L_0} = \frac{\Delta L}{L_0} \tag{2.3}$$

Tensile Strength, σ, (MPa) is the maximum tensile stress, which a material is capable of developing. It is calculated from the maximum load carried during a tension test and the original cross-section area of the specimen.

Tensile Modulus (Young's Modulus), E, (MPa) is the ratio of stress to corresponding strain below the proportional limit of a material.

$$E = \frac{\sigma}{\varepsilon} \tag{2.4}$$

To measure tensile modulus, the same thing will be done to measure strength and ultimate elongation. The amount of stress will be increased slowly, and then elongation at break will be measured that the sample undergoes at each stress level till the sample is broken. Then a plot of stress versus elongation, as shown in Figure 2.14 will be prepared. Another typical drawing can be seen in Figure 2.15. This plot is called a stress-strain curve. The height of the curve when the sample breaks is the tensile strength, of course, and the tensile modulus is the slope of this plot. If the slope is steep, the sample has a high tensile modulus, which means it resists deformation. If the slope is gentle, then the sample has a low tensile modulus, which means it is easily deformed.

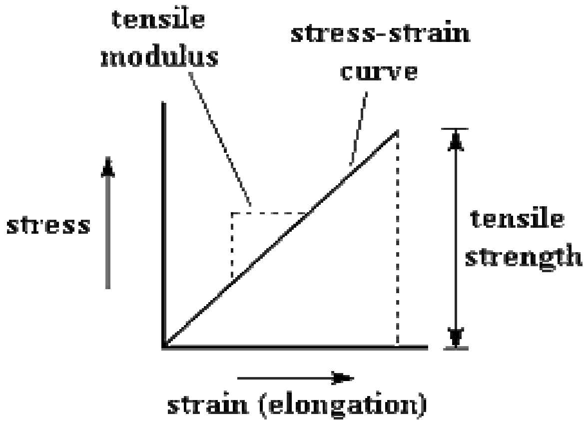


Figure 2.14 Representation of stress-strain behavior

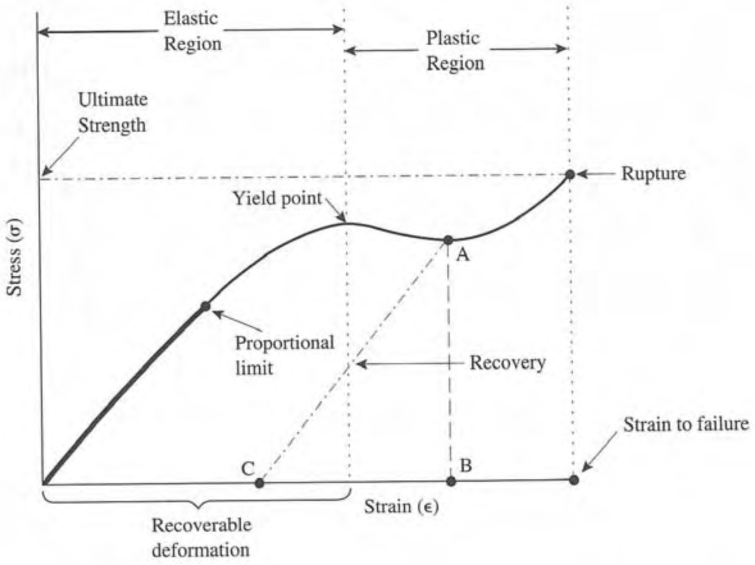


Figure 2.15 Stress-strain behavior over the entire strain range for a typical polymeric material [24]

2.9.1.2 Flexural Properties

In flexural tests, a rod specimen having either a circular or rectangular cross-section is bent until fracture, using a three or four point loading technique (Figure 2.16).

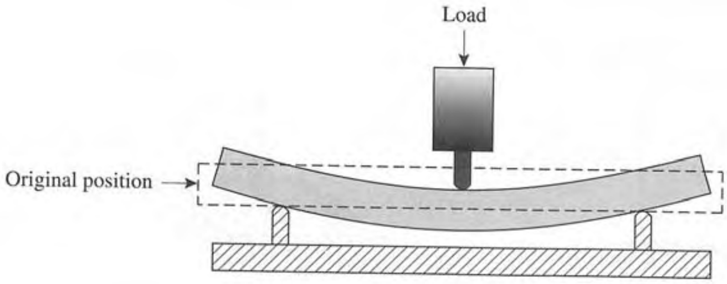


Figure 2.16 Flexural test procedure.

In three-point loading, which was applied in this thesis, the top surface of the specimen is placed in a state of compression, whereas the bottom surface is tension. Stress is computed from the specimen thickness, the bending moment, and the moment of inertia of the cross-section. The maximum tensile stress exists at the bottom specimen surface directly below the point of load application.

The stress at fracture using this flexural test is known as the flexural strength. For a rectangular cross-section, the flexural strength, σ_{fs}, is equal to:

$$\sigma_{fs} = \frac{3F_f L}{2bd^2} \qquad (2.5)$$

where F_f is the load at fracture (N), L is the distance between support points (mm), b is the width of the specimen (mm), and d is the depth of specimen (mm).

The maximum strain in the outer fibers occurs at midspan, is calculated as follows:

$$r = \frac{6Dd}{L^2} \qquad (2.6)$$

where r is the maximum strain in the outer fibers (mm/mm), D is the maximum deflection of the center of the beam (mm), L is support span (mm) and d is the depth of specimen (mm).

Tangent modulus of elasticity (flexural modulus), E_B is the ratio within the elastic limit of stress to corresponding strain and will be expressed as MPa. It is designated by drawing a tangent to the steepest initial straight-line portion of the load-deflection curve by using the following equation:

$$E_B = \frac{L^3 m}{4bd^3} \qquad (2.7)$$

where E_B is modulus of elasticity in bending (MPa), L is the length of support span (mm), b is the width of the beam tested (mm), d is the depth of beam tested (mm), and m is the slope of the tangent to the initial straight-line portion of the load deflection curve, N/mm of deflection.

2.9.1.3 Impact Properties

Impact tests are high-speed fracture tests that measure the energy to break a specified specimen. In the Izod and Charpy impact tests, a pendulum with hammer like weight strikes a specimen (a notched or unnotched bar), and the energy required to break the specimen is determined from the loss in kinetic energy of the weight.

2.9.1.4 Standard Deviation

All results obtained from mechanical tests are resulted with their standard deviation. Standard deviation is calculated from the formula below.

$$s = \sqrt{\frac{\sum X^2 - n\bar{X}^2}{n-1}} \qquad (2.8)$$

where s is the estimated standard deviation, X is the value of single observation; n is the number of observations and $\bar{X}$ is the arithmetic mean of the set of observations.

2.9.2 Scanning Electron Microscopy (SEM)

Some of the structure elements are too fine or small to examine by using optical light microscopy. In case of such circumstances, the electron microscope, which is capable of much higher magnifications, shall be employed.

In SEM analysis, the surface of the specimen is coated with a gold-platinum including solution with a sputter coater under vacuum firstly. This is due to make the specimen surface conductive in order to obtain electron reflection. Then the specimen is placed into the SEM and the surface of the specimen is scanned with an electron beam, and the reflected (or back-scattered) beam of electrons is collected, and then displayed at the same scanning rate on a cathode ray tube. The image on the screen, which may be digitized, represents the surface features of the specimen. Magnifications ranging from 10 to in excess of 500 000 diameters are possible.

2.9.3 Differential Scanning Calorimetry (DSC)

Thermal analysis of polymeric materials could be done by various methods such as thermal gravimetric analysis, differential thermal analysis and differential scanning calorimetry (DSC).

The most popular DSC design, two pans sit on a pair of identically positioned platforms connected to a furnace by a common heat flow path (Figure 2.17). In one pan polymer sample is put. The other one is the reference pan and left as empty. Then the computer is turned on the furnace, and tells to heat the two pans at a specific rate, usually something like 10 ^{o}C per minute. The computer makes sure that the two separate pans heat at the same rate as each other. The two pans are different. One has polymer in it, and one does not. The polymer sample means there is extra material in the sample pan. Having extra material means that it will take more heat to keep the temperatures of the sample pan increasing at the same rate as the reference pan. Additional heat is what is measured in a DSC analysis. Computer makes a plot as the temperature increases. On the x-axis it plots the temperature. On the y-axis it plots the difference in heat flow between the sample and reference.

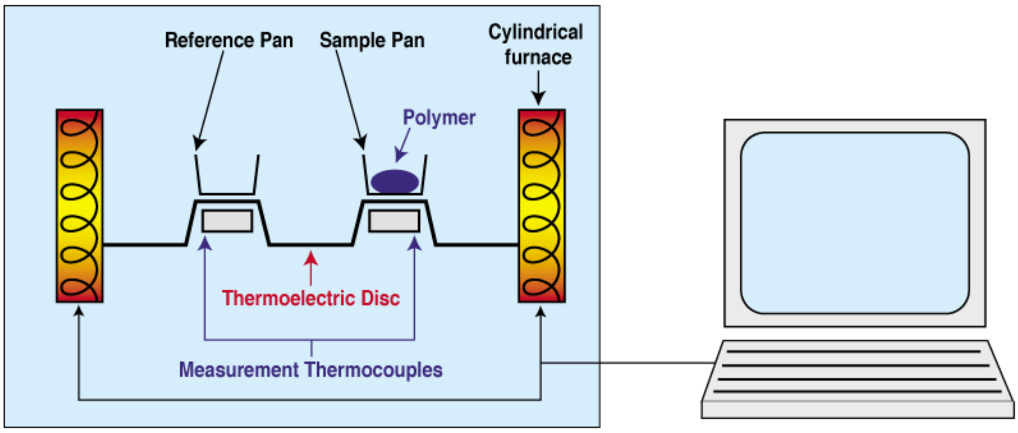


Figure 2.17 Representative drawing of differential scanning calorimeter

Differential scanning calorimetry (DSC), is a technique of nonequilibrium calorimeter, in which the heat flow into or away from the polymer compared with the heat flow into or away from a reference is measured as a function of temperature. The thermodynamic property monitored here is enthalpy. When the sample undergoes a thermal transition, the power to the two heaters is adjusted to maintain their temperatures, and a signal proportional to the power difference is plotted on the second axis of the recorder. The area under the resulting curve is a direct measure of the heat of transition. Thermal characteristics of polymers such as T_g and T_m can easily be determined by using this method.

2.9.4 Melt Flow Index

Rather than attempt to determine the average molecular weight and the molecular weight distribution, either by calculation or by using some experimental methods, many important flow characteristics of the polymer, which are strongly dependent on these properties, can be found using a simple test called the melt flow index. In fact, the melt index is one of the most common parameters specified when describing a polymer.

In the melt flow index test, a large block of metal in which heating coils have been imbedded surrounds a tube into which several grams of the polymer material to be tested are placed. The desired temperature for the test is selected and the apparatus (Figure 2.18) is brought to this temperature. A weighted piston is then placed in the tube so that it applies a constant for on the polymer. To avoid confusion, the temperature and weight conditions are reported with the results of the test.

Under the constant temperature and weight that is appropriate for the type of polymer to be tested, the polymer eventually begins to flow slowly out the small orifice at the bottom of the tube. When this flow is constant, a stop watch is started and after a set amount of time, extrudate that has come out during the set time is carefully removed and weighed. The weight of the material extruded during the specified time is the melt index expressed in grams per 10 minutes.

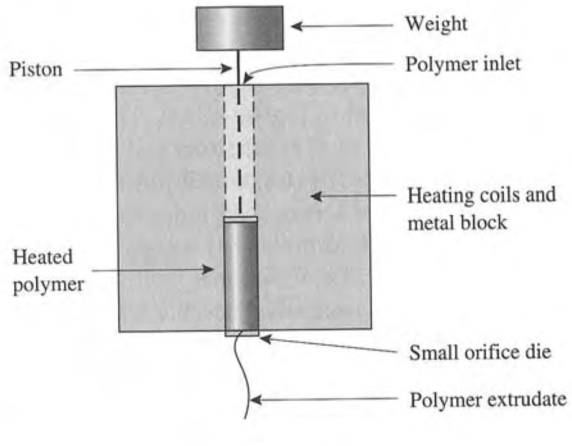


Figure 2.18 Schematic drawing of melt flow index apparatus

The melt index is not an intrinsic or fundamental property of a polymer. It is rather, a convenient method for expressing important flow characteristics of the polymer which clarifies the way in which can be processed. A high melt flow index indicates a low molecular weight. The opposite is also true. Also polymers with a low melt flow index flow slowly and have a high viscosity.

As with the relationship between molecular weight and mechanical properties, the relationship between molecular weight and melt flow index is also nonlinear.

2.10 Previous Studies

Ismat et. al. [33] studied the impact modification of recycled PET obtained from beverage and textile industry. In this study they added polyester elastomers to amorphous, crystalline and recycled PET. These elastomers contain a copolymer of n-butyl terephthalate as hard segment and ethylene oxide as the soft segment. Their core structure is the butyl acrylate/methyl methacrylate. They also added compatibilizers, antioxidants and glass fiber as filler material. Samples were prepared in a viscometer at 75 rpm and at 271 °C, and then were compression molded for determining tensile properties and molecular weight distribution. NMR characterization was also performed. The samples were injection molded at a heating range 250-271 °C. Tensile and flexural tests were applied at room temperature. Impact tests were done by using Izod impact test method. In conclusion, they claimed that increase in melt viscosity increased the molecular weights of the composites. The maximum impact strength was observed at composite including 35 % poly(butyl acrylate) polyester. Also they reported that impact strength of PET tended to decrease with increasing polyacrylate content.

Luethi et. al. [34] studied the push-out tests on weft-knitted glass fiber reinforced PET. In this study, they developed a model for the determination of debonding energy and fit the experimental data to that model. The results were satisfactory and the showed that the predicted model was valid. They also calculated the asperity friction, coefficient of friction and thermal clamping stress.

Incarnato et. al. [35] studied the effect of pyromellitic dianhydride (PMDA) on the molecular weight of recycled PET. In this scope, they mixed PMDA with recycled PET in a single screw extruder at 280 °C and 40 rpm. The PMDA contents were 0.25 %, 0.5 %, 0.75 % and 1 % (by weight) respectively in each run. In conclusion, they claimed that PMDA acted as a good chain extender and increased the molecular weight of recycled PET in some extent. The maximum properties were obtained at 0.75 % PMDA including recycled PET. Addition of PMDA made recycled PET suitable for film blowing and blow molding.

Pawlak et. al. [15] characterized the recycled PET in Middle Europe and European Community. In this manner, they collected recycled PET from three different companies and recycled PET-polyolefin mixture from another company. In order to characterize the samples they made TGA, DSC, FTIR analyses and also determined the tensile strength, dynamic viscosities, intrinsic viscosities of the samples. They concluded that all samples included approximately 0.1-5 % other polymers. Also all samples contained some amount of PVC and PVC content exceeding 50 ppm makes recycled PET unsuitable for advanced applications like film forming. This is due to the hydrolysis reactions that are catalyzed above 50 ppm of PVC and also PVC reduces the durability of the recycled PET. They also claimed that addition of polymers to recycled PET without compatibilizers deteriorated tensile properties.

Papke et. al. [36] studied the effect of thermoplastic elastomers on PET. They mixed 50 wt. % PET with 30 wt. % glycidyl methacrylate grafted rubber (compatibilizer) and with 20 weight percent various rubbers. In this study, they used EPR, EPDM, NBR-1, NBR-2, E/αO-1, E/αO-2 and EGMA type rubbers. They concluded that, EGMA was more compatible with PET rather than EPR type rubber. They also claimed that the best mechanical properties were observed with the usage of NBR types of rubbers. In order to analyze the morphology of the blends they drawn torque versus time, temperature versus time plastograms. They obtained significant torque increase for blends including EPDM and NBR types of elastomers.

Li et. al. [37] investigated the effect of microfiber reinforcement on morphologies of PET/PE. Composites were prepared through slit-die extrusion and hot-stretching and then molded by using injection molding technique. Composites were molded below the melting point of PET in order to keep the fibers in the matrix. In the study, they changed the PET/PE weight percent and investigated the basic microfiber properties such as diameter, and diameter distribution. They concluded that with the increase of PET content, diameter of the fiber increased and diameter distribution widened, but minimum fiber diameter remained constant.

Loyens et. al. [38] studied the mechanical properties of rubber toughened semicrystalline PET at room temperature. Ethylene-co-propylene rubber (EPR), maleic anhydride grafted EPR (EPR-g-MA), glycidyl methacrylate grafted EPR (EPR-g-GMA_x) and ethylene-glycidyl methacrylate copolymers (E-GMA_x) are used as different types of elastomers. For the preparation of blends, firstly a preblending was done in a batch mixer at 180 °C and 50 rpm for 5 minutes and blends were pelletized. Further blending was done at 280 °C and 50 rpm for 10 minutes. The samples were compression molded at 280 °C. DSC analyses and impact tests were performed. They concluded that maleic anhydride grafted elastomers did not affect impact strength unlike glycidyl methacrylate grafted elastomers. Impact strength increased with the better dispersion of elastomer in the PET matrix.

Lee et. al. [39] studied the effects of vacuum, mold temperature and cooling rate on mechanical properties of press consolidated glass/fiber composites. They investigated the morphology, tensile properties and degree of crystallinities of the composites. They prepared samples by putting 4 PET films between each of 8 glass fiber films, that formed a composite containing 36 films and they were processed by rapid press consolidation technique (RPCT). They changed the process parameters of RPCT, such as vacuum degree, mold temperature and cooling rate, and examined the effect of them. In conclusion, they mentioned that the increase of vacuum rate increased the tensile strength of the composites. They claimed that when cooling rate decreased, degree of crystallinity also decreased. Also composites became more brittle and tensile modulus increased with decreasing cooling rate.

Arencon et. al. [40] studied the effect of injection molding process parameters and effect of nucleating agents on glass fiber-PET composites. They mixed PET with E-type glass fiber in a twin screw extruder and added sodium benzoate and titanium benzoate as nucleating agents. The temperature profile was 190-250-270-270-270-270-270 °C and screw speed was 230 rpm. Then, extrusion pellets were injection molded at a temperature profile of 220-250-270-270-270 °C with an injection pressure of 80 bar and a back pressure of 10 bar. The investigated injection molding parameters were mold temperature, pressure apply time and mold close time. DSC analyses and tensile tests for thermal and mechanical properties of composites were performed respectively. They concluded that mold temperature and mold close time significantly affected the crystallinity of the composites. With the increase of pressure apply time, composites' tensile strength and elongation at break values increased. Sodium benzoate found as a better nucleating agent rather than titanium benzoate, but significantly decreased the tensile strength of the composites.

Chaudhari et. al. [2] made the impact modification of waste PET by polyolefinic elastomer. They investigated both the effect of elastomer content, which is a terpolymer of ethylene, and effect of the compatibilizer content, which is poly(ethylene-co-acrylic acid) EAA. Bottle grade recycled PET was first extruded in a twin screw extruder and pelletized. The temperature profile was 180-200-220-230-248 °C and screw speed was 60 rpm. After that it was blended with an elastomer that is a copolymer of ethylene, in a twin screw extruder with a temperature profile of 190-210-230-245-250 °C and a screw speed of 80 rpm. Final pellets were injection molded at a pressure of 85 kg/cm^2 and a temperature profile of 240-255-268 °C. In order to characterize the mechanical, thermal and morphological properties, tensile and flexural tests; DSC analyses and SEM analyses were performed. Also viscosities of the blends were determined. They concluded that with the increase of elastomer content from 2 % to 10 % impact strength increased significantly, but flexural modulus and tensile strength decreased. When the compatibilizer content doubled, impact strength also increased significantly. As a result of elastomer addition, degree of crystallinity of recycled PET decreased. Viscosities of the blends increased with the increase of elastomer content, and compatibilizer favored this trend more strongly.

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Recycled PET

Recycled PET, which was used during the experiments, was supplied by SaSA-DupontSA Company, Adana. Recycled PET was in the form of randomly sized flakes and obtained from bottles. Some basic properties of the recycled PET are given Table 3.1:

Table 3.1 Properties of the recycled PET

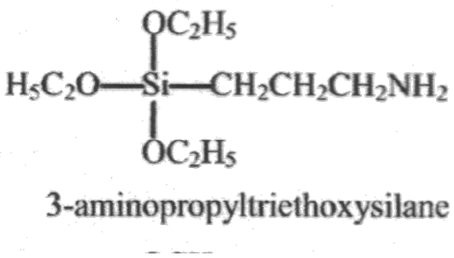
Property	
PVC Content	60 ppm
Polyethylene Content	5 ppm
Metal Content	0 ppm
Glue Content	10 ppm
Paper Content	3 ppm
Intrinsic Viscosity	0.75 dl/g
Glass Transition Temperature	60 °C
Melting Temperature	255 – 260 °C

3.1.2 Glass Fiber

The glass fiber used in the experiments was obtained from Cam Elyaf A.Ş., Gebze. Its trade name is “PBT-2” and it is a E-type short glass fiber. It was coupled with a silane based coupling agent and also includes epoxy film former. The properties of the glass fiber are given in Table 3.2 and the chemical structure of coupling agent is shown in Figure 3.1.

Table 3.2 Properties of the glass fiber

Property	
Trade Name of the Fiber	PBT-2
Glass Type	E Type
Fiber Length	4.5 mm
Fiber Diameter	10.5 μ (nominal)
Coupling Agent Type	Silane
Coupling Agent	3-aminopropyltriethoxysilane
Coupling Agent Amount	0.1 %



$$H_5C_2O{-}\underset{\displaystyle OC_2H_5}{\overset{\displaystyle OC_2H_5}{Si}}{-}CH_2CH_2CH_2NH_2$$

Figure 3.1 Chemical structure of 3-aminopropyltriethoxysilane

3.1.3 Impact Modifier (Elastomer)

In this study, Lotader AX8900, which is a terpolymer of ethylene/methyl acrylate/glycidyl methacrylate (E-MA-GMA), was chosen for the impact modification of recycled PET. It was purchased from Atofina Chemicals Inc., France. It is in form of small pellets, and solid at room temperature. Chemical structure and specifications of the elastomer are represented in Figure 3.2 and Table 3.3.

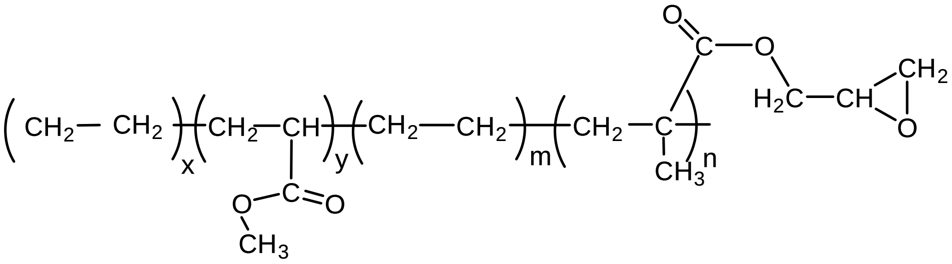


Figure 3.2 Chemical structure of Lotader AX8900

Table 3.3 Specifications of Lotader AX8900

Property	E-MA-GMA
Trade Name	Lotader AX8900
Methyl Acrylate Content	25 wt. %
Glycidyl Methacrylate Content	8 wt. %
Melt Flow Index (190°C, 2.1 kg ASTM D 1238)	6 g/10 min
Melting Temperature (DSC)	65 °C
Vicat Softening Temperature (ASTM D1525-1 kg)	< 38 °C
Tensile Strength (ASTM D 638)	6 MPa
Elongation at break (ASTM D 638)	1000 %
Hardness	70 Shore A

3.1.3.1 GMA Functionality

Glycidyl Methacrylate (GMA) monomer (Figure 3.3) contains both acrylic and epoxy groups, providing the design and performance versatility required for the most demanding coating and resin applications.

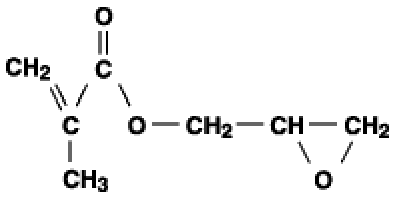


Figure 3.3 Molecular structure of glycidyl methacrylate.

3.1.3.2 Acrylic and Vinyl Functionality

These functionalities allow copolymerization with a variety of other vinyl monomers in aqueous and nonaqueous systems. Resulting polymers feature a unique combination of epoxy functionality with an acrylic backbone. Wide co-monomer selection provides easy control of physical and chemical properties such as T_g and solution viscosity.

3.1.3.3 Epoxy Functionality

This functionality enables crosslinking reactions with amines, carboxylic acids, anhydrides and hydroxyl-containing polymers. Proper accelerator/catalyst choice allows use of a wide range of cure temperatures and schedules. Epoxy group allows structural modification of the polymer backbone that can result in differentiated properties and higher performance.

Some GMA reactions with methacrylate and epoxide groups are shown in Figure 3.4 and 3.5

Typical GMA Reactions

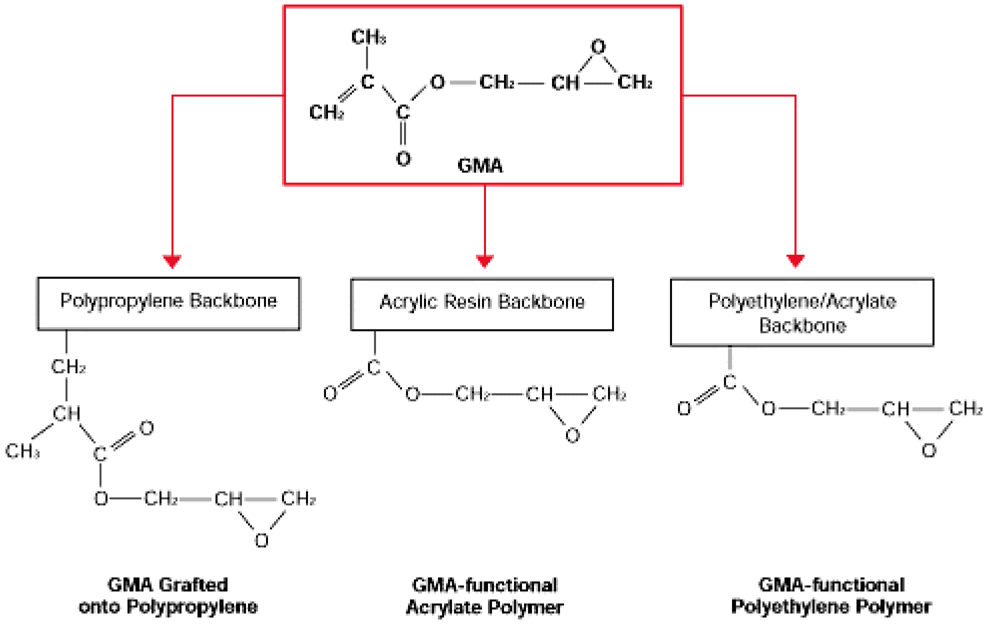


Figure 3.4 Typical GMA reactions with methacrylate group

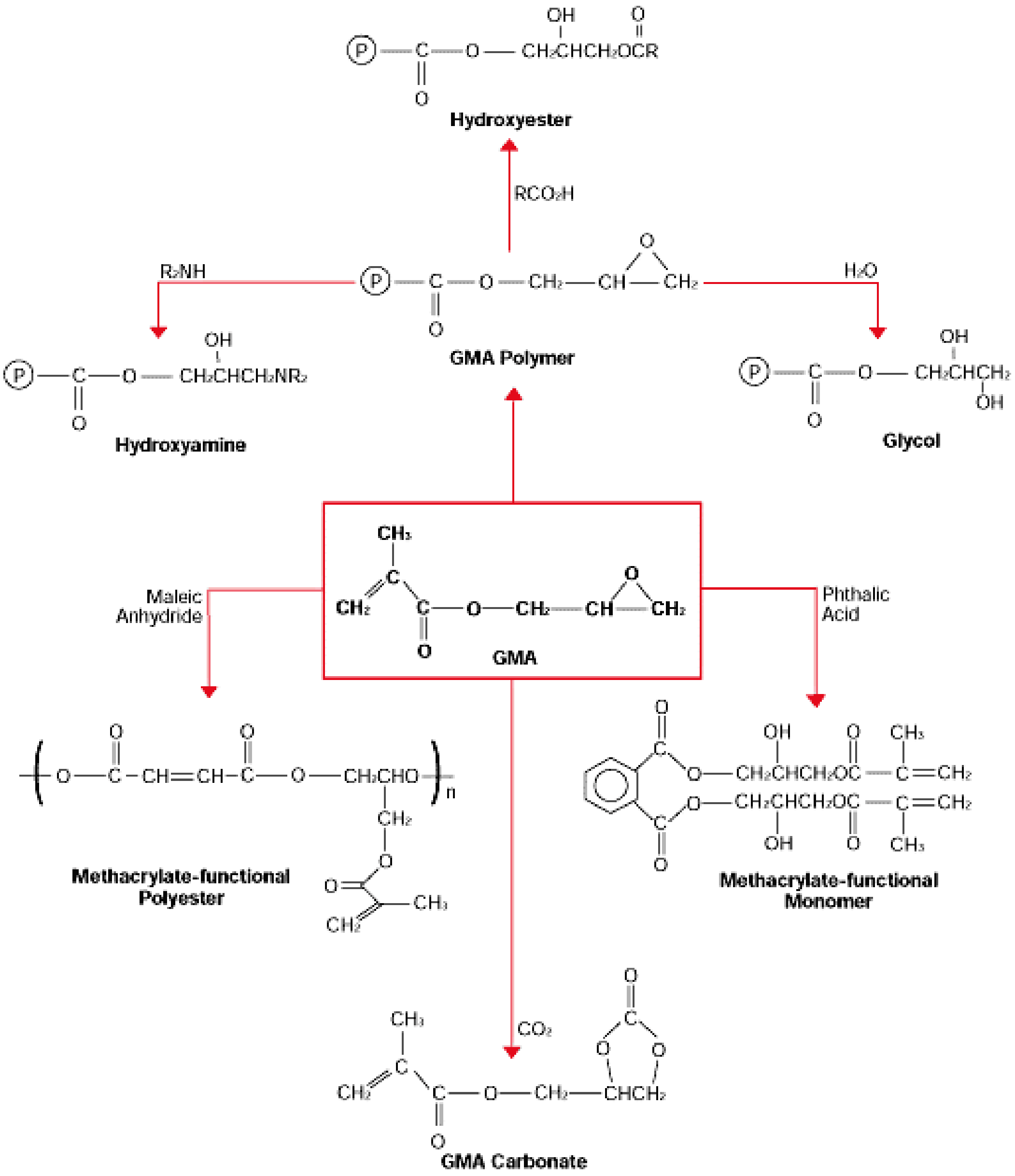


Figure 3.5 Typical GMA reactions with epoxide group

3.1.3.4 Other Elastomers Used in This Study

In the further stages of this thesis effect of elastomer type on ternary composites were investigated. This was done especially to give ideas for further studies. In this investigation instead of Lotader AX8900, four different elastomers were tried. Their trade names are Elvaloy PTW, Elvaloy 1224 AC, Lotader AX8840, Lotryl 28 MA 07. The first two were procured from Dupont Chemicals Company, USA. The last two elastomers were obtained from Atofina Chemicals, France. Elvaloy PTW and Lotader AX8840 include different amounts of glycidyl methacrylate group; Elvaloy 1224 AC and Lotryl 28 MA 07, do not have glycidyl methacylate group. Lotryl 28 MA 07 has nearly same properties as Lotader AX8900 except the functional group. It was chosen for comparison purposes and in order to determine whether, there is a reaction between elastomer and matrix. Their properties are given in Tables 3.4 - 3.7. All elastomers are in form of pellets and solid at room temperature. Chemical structures of Elvaloy PTW and Elvaloy 1224 AC, Lotryl 28 MA 07 are also given in Figures 3.6, 3.7 and 3.8.

Table 3.4 Properties of Elvaloy PTW Elastomer

Property	Values
Content	Glycidyl Methacrylate nButyl Acrylate
Melt Flow Index	12 g/10 min
Tensile Strength	5.1 MPa
Elongation at break	950 %
Hardness (Shore A-2)	73
Melting Point	72 °C
Freezing Point	50 °C

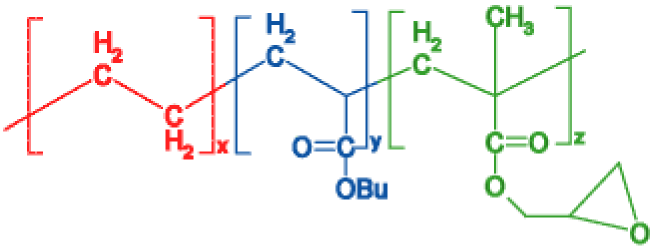


Figure 3.6 Chemical structure of Elvaloy PTW

Table 3.5 Properties of Elvaloy 1224 AC Elastomer

Property	Values
Content	Methacrylate (24 wt. %)
Melt Flow Index	2 g/10 min
Tensile Strength	12 MPa
Elongation at break	846 %
Density	944 kg/m^3
Hardness (Shore A-2)	78
Melting Point	91 °C

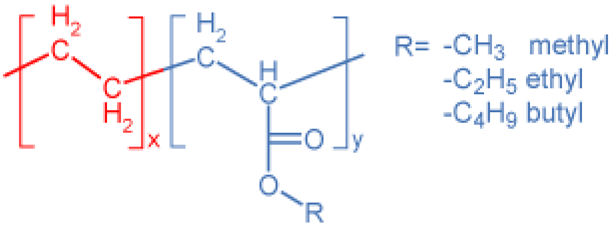


Figure 3.7 Chemical structure of Elvaloy 1224 AC

Table 3.6 Properties of Lotader AX8840 Elastomer

Property	Values
Content	Acrylic Ester (0 wt. %) Glycidyl Methacrylate (8 wt. %)
Melt Flow Index	5 g/10 min
Tensile Strength	8 MPa
Elongation at break	420 %
Hardness (Shore A-2)	92
Melting Point	109 °C

Table 3.7 Properties of Lotryl 28 MA 07 Elastomer

Property	Values
Content	Acrylic ester (28 wt. %)
Melt Flow Index	7 g/10 min
Tensile Strength	7 MPa
Elongation at break	846 %
Density	950 kg/m^3
Hardness (Shore D)	76
Melting Point	65 °C

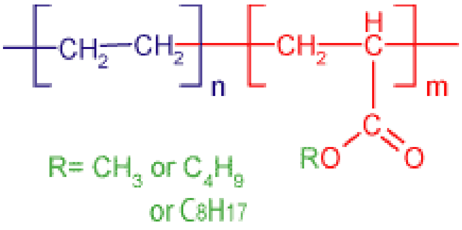


Figure 3.8 Chemical structure of Lotryl 28 MA 07

3.2 Preparation of Specimens

3.2.1 Twin Screw Extrusion

In this study, a Thermo Prism TSE 16 TC twin screw extruder was used for the preparation of all the blends/composites. The specifications of the extruder are given in Table 3.8.

Table 3.8 Specifications of the Twin Screw Extruder

Property	
Model	Thermo Prism TSE 16 TC
Type	Twin Screw
Screw Type	Corotating
Twin Bore Diameter	16 mm
Screw Diameter	15.6 mm
Maximum Screw Speed	500 rpm
Barrel Length	384 mm (24 D)
Die Length	16 mm (1 D)
Maximum Torque	12 Nm

For different set of experiments several process parameters were tried during extrusion and they will be mentioned further. Figure 3.9 represents the schematic drawing of the extruder which was used.

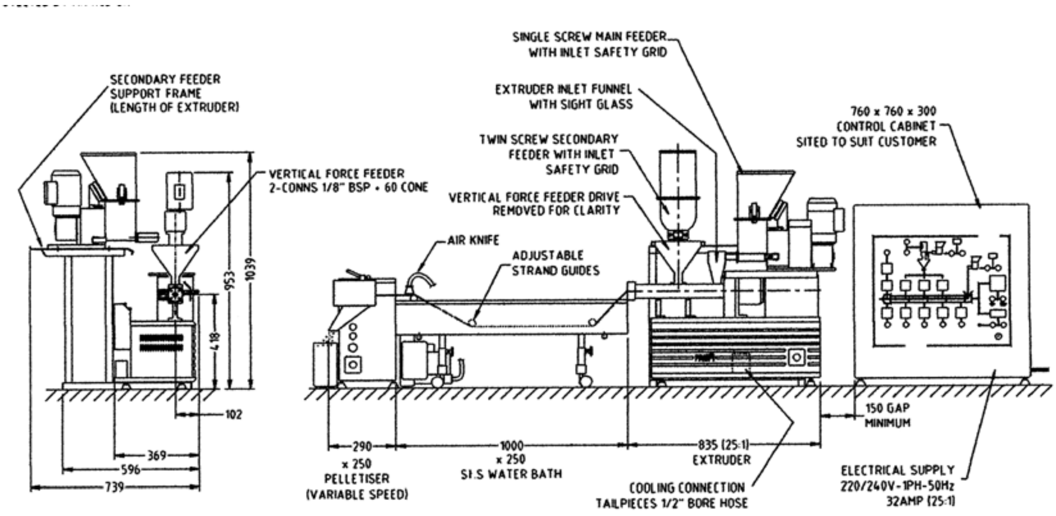


Figure 3.9 Thermo Prism TSE 16 TC twin screw extruder

3.2.2 Injection Molding

A laboratory scale injection molding machine (Microinjector, Daca Instruments) shown in Figure 3.10 was used to mold pure recycled PET. Molding parameters given in Table 3.9 were kept constant throughout the molding process.

Water was used as a coolant for the mold temperature controller, which was connected to the mold in order to maintain a constant and specific mold temperature.

In this study, injection molding was used to prepare pure recycled PET rather than compression molding, since in compression molding samples were cut by knifes from plates and it is not possible to cut them due to brittle structure of PET.

Table 3.9 Molding parameters for Injection Molding

Injection Molding Parameters	Unit	Value
Nozzle Temperature	°C	275
Mold Temperature	°C	18
Fill Time	sec.	30
Hold Time	min.	1
Injection Speed	---	Fast
Injection Pressure	bar	8

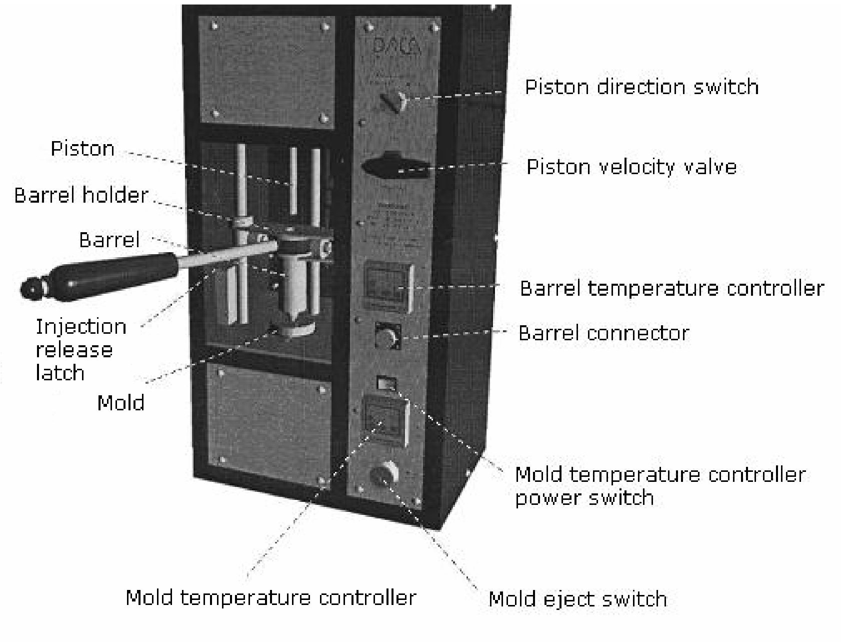


Figure 3.10 Injection molding machine

3.2.3 Compression Molding

A hydraulic compression molding machine was used in order to prepare the test specimens except pure recycled PET. During compression molding, selected mold parameters were kept constant. The parameters are given in Table 3.10 and a drawing for the machine is shown in Figure 3.11.

Table 3.10 Molding parameters for Compression Molding

Compression Molding Parameters	Unit	Value
Molding Temperature	°C	280
Oil Pressure	bar	150
Mold Pressure	bar	7.2
Pre-heating Time	min.	5
Heating Time	min.	8
Cooling Method	---	Quenching

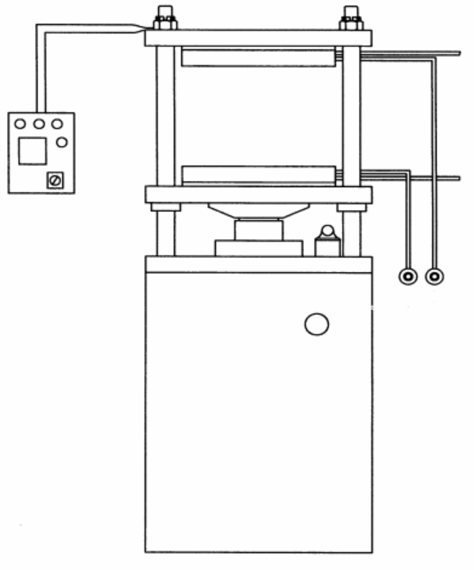


Figure 3.11 Compression molding machine

3.2.4 Experimental Procedure

In this study, in all sets of experiments samples were dried prior to mixing in extrusion. Then they were mixed in a twin screw extruder and pelletized. Before molding, all samples were dried at 120 °C for 4 hours. Samples were compression molded in order to prepare specimens for mechanical testing, thermal and morphological characterization. This procedure is illustrated in Figure 3.12. Some minor changes were done when needed and they will be mentioned further

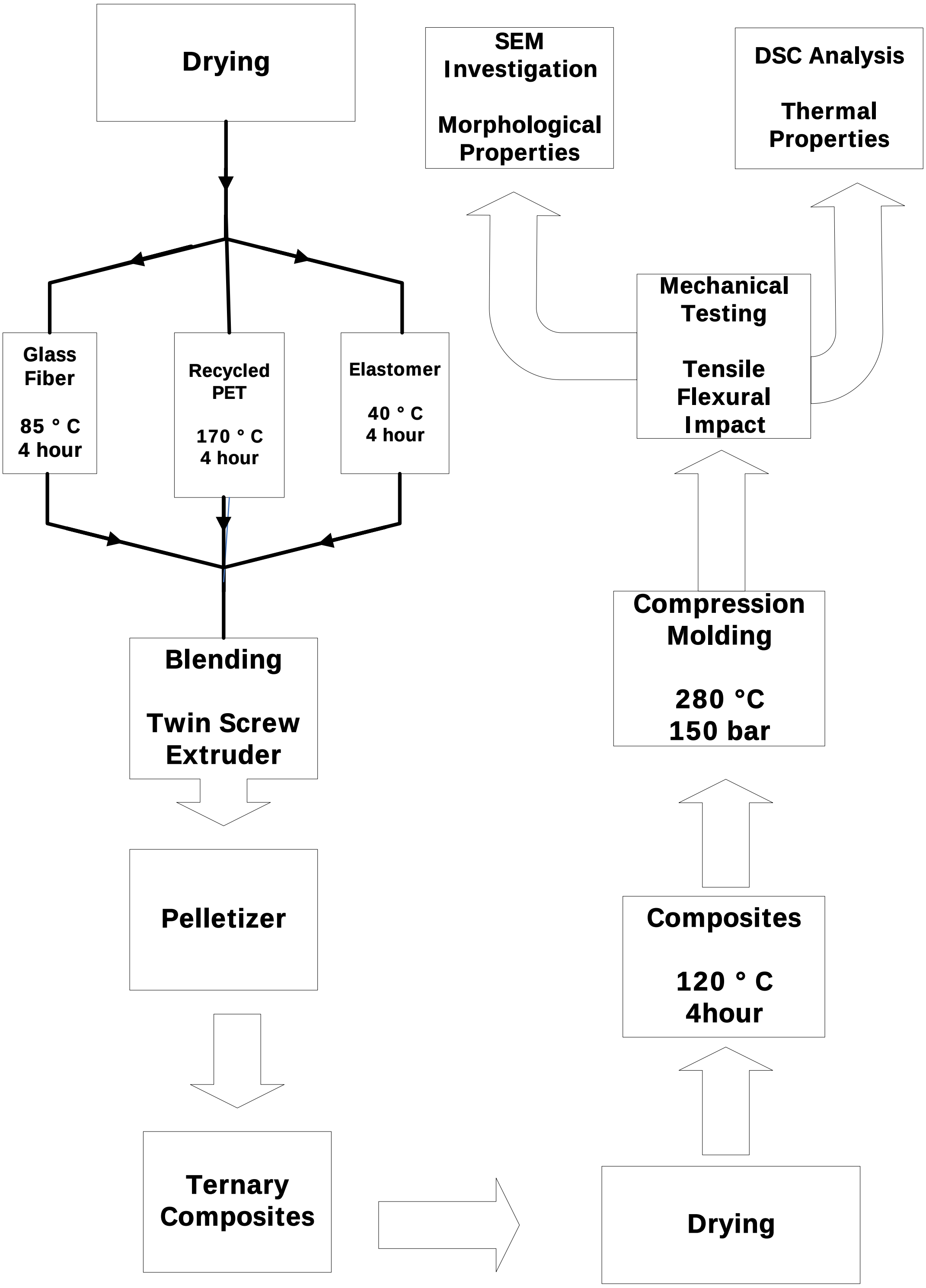


Figure 3.12 General experimental procedure

This is the general experimental procedure followed during the experiments.

In this study, the main concern is to produce the ternary composites including glass fiber, elastomer and recycled PET, but besides this, several set of experiments were performed in order to determine effects of process and material parameters on final properties of the materials.

Before each run of each set of experiments, the raw materials were dried in order to prevent the hydrolytic degradation in extrusion. The materials were dried before extrusion and also before molding. Drying procedure is summarized in Table 3.11.

Table 3.11 Drying procedure of the materials.

Material Type	Drying Temperature (°C)	Drying Time (h)
Recycled PET	170	4
Glass Fiber	85	4
Elastomer	40	4

Prior to either compression or injection molding, all composites/blends after extrusion were dried at 120 °C for 4 hours.

In the following sections, the different sets of experiments that were done during this thesis are explained.

3.2.4.1 Set I: Preparation of pure recycled PET

In this set, the mechanical properties of pure recycled PET were determined in order to use this information for comparison in the further stages of the experiments. To prepare the specimens recycled PET, which was extruded at 220-275-280-285-290 °C temperature profile and with a screw speed of 230 rpm, was molded by using injection molding technique. Compression molding technique could not be used for preparation of pure recycled PET since the samples can not be cut due to brittle structure of PET. In order to get rid off this problem injection molding technique was applied. The injection molding parameters were kept constant as given in Table 3.9.

3.2.4.2 Set II: Preparation of binary composites of recycled PET and glass fiber with different glass fiber contents

In this set, recycled PET was mixed with glass fiber from 10 wt. % to 50 wt. % with a 10 % increase each time. Required drying was done according to Table 3.11. After that the samples were extruded in the twin screw extruder with the following extrusion parameters:

Table 3.12 Extrusion process parameters

Parameters	Temperature Profile				
	Hopper	2. Zone	3. Zone	4. Zone	Die
Temperature (°C)	220	275	280	285	290
PET Feed Rate (g/min)	20				
Screw Speed (rpm)	230				

During extrusion, recycled PET was fed from the main feeder and the glass fiber was fed from the side feeder. The composites were then compression molded according to the process parameters given in Table 3.10, after drying. With the proper knives, specimens for tensile, flexural and impact tests were obtained.

3.2.4.3 Set III: Preparation of binary blends of recycled PET and elastomer with different elastomer contents

In this set, recycled PET was mixed with elastomer from 10 wt. % to 50 wt. % with a 10 % increase in each time. Required drying was done according to Table 3.11. After that the samples were extruded in the twin screw extruder with the same extrusion parameters given in Table 3.12. Material addition sequence and preparation technique were same as the ones explained in Set II.

3.2.4.4 Set IV: Preparation of glass fiber-recycled PET composites with different processing parameters

In this set, effects of selected extrusion parameters on glass fiber-recycled PET composites were examined. For this purpose, 30 % glass fiber-70 % recycled PET composite was chosen. At this composition, effects of screw speed and temperature profile during extrusion were studied. Required drying was done according to conditions given in Table 3.11. After that the samples were extruded in the twin screw extruder with the following extrusion parameters given in Tables 3.13 – 3.18.

Table 3.13 Extrusion parameters for low screw speed rate at constant temperature profile

Parameters	Temperature Profile				
	Hopper	2. Zone	3. Zone	4. Zone	Die
Temperature (°C)	220	275	280	285	290
PET Feed Rate (g/min)	20				
Screw Speed (rpm)	170				

Table 3.14 Extrusion parameters for normal screw speed rate at constant temperature profile and for normal temperature profile at constant screw speed

Parameters	Temperature Profile				
	Hopper	2. Zone	3. Zone	4. Zone	Die
Temperature (°C)	220	275	280	285	290
PET Feed Rate (g/min)	20				
Screw Speed (rpm)	230				

Table 3.15 Extrusion parameters for high screw speed rate at constant temperature profile

Parameters	Temperature Profile				
	Hopper	2. Zone	3. Zone	4. Zone	Die
Temperature (°C)	220	275	280	285	290
PET Feed Rate (g/min)	20				
Screw Speed (rpm)	290				

Table 3.16 Extrusion parameters for low temperature profile at constant screw speed

Parameters	Temperature Profile				
	Hopper	2. Zone	3. Zone	4. Zone	Die
Temperature (°C)	210	265	270	275	280
PET Feed Rate (g/min)	20				
Screw Speed (rpm)	230				

Table 3.17 Extrusion parameters for high temperature profile at constant screw speed

Parameters	Temperature Profile				
	Hopper	2. Zone	3. Zone	4. Zone	Die
Temperature (°C)	230	285	290	295	300
PET Feed Rate (g/min)	20				
Screw Speed (rpm)	230				

In extrusion, recycled PET and glass fiber were fed from the main feeder and from the side feeder, respectively. Dried composites were then compression molded according to the process parameters given in Table 3.10. Specimens for tensile, flexural and impact tests were cut with the proper knives.

3.2.4.5 Set V: Preparation of elastomer-recycled PET blends with different processing parameters

In this set, effects of selected extrusion parameters, such as processing temperature and screw speed on elastomer-recycled PET blends were examined. For this purpose, 30 % elastomer-70 % recycled PET blend was chosen. Conditions given in Table 3.11 were used for required drying. After that, the samples were prepared in the twin screw extruder according to the given extrusion parameters in Tables 3.13 – 3.17.

Same material addition sequence and specimen preparation techniques as used in Set IV were applied to the blends prepared in Set V.

3.2.4.6 Set VI: Preparation of elastomer-glass fiber-recycled PET ternary composites

In this set, elastomer-glass fiber-recycled PET ternary composites were prepared by using the twin screw extruder at a wide range of different compositions of glass fiber and elastomer. Required drying was done according to the information in Table 3.11. Table 3.18 shows the processing conditions during extrusion of the composites. Selected compositions are given in Table 3.19.

Table 3.18 Extrusion parameters for ternary composites

Parameters	Temperature Profile				
	Hopper	2. Zone	3. Zone	4. Zone	Die
Temperature (°C)	220	275	280	285	290
PET Feed Rate (g/min)	Variable for each composition				
Screw Speed (rpm)	200				

Table 3.19 Compositions of the produced ternary composites

Sample	% Elastomer	% Glass Fiber	% Recycled PET
S_1	10	10	80
S_2	10	20	70
S_3	10	30	60
S_4	10	40	50
S_5	20	10	70
S_6	20	20	60
S_7	20	30	50
S_8	20	40	40
S_9	30	10	60
S_{10}	30	20	50
S_{11}	30	30	40
S_{12}	40	10	50
S_{13}	40	20	40
S_{14}	50	10	40

During extrusion, recycled PET-elastomer mixture, which was dry blended before, was fed from the main feeder and glass fiber was fed from the side feeder. The produced composites were prepared by using the compression molding machine for characterization experiments.

3.2.4.7 Set VII: Preparation of ternary composites with different types of elastomers

In this set, effects of different types of elastomers on elastomer-glass fiber-recycled PET ternary composites were examined. For this purpose, 20 % elastomer-20 % glass fiber-60 % recycled PET composite was chosen, due to its reasonable mechanical properties. At this composition, other than our primary elastomer Lotader AX8900, four different elastomers, which were mentioned before in this chapter, were tried. Required drying was done according to the conditions in Table 3.11. After that, the samples were extruded in the twin screw extruder according to the given extrusion parameters in Table 3.18.

Same procedure of addition sequence and specimen preparation given in Set VI was used for the ternary composites with different elastomers.

3.2.4.8 Set VIII: Preparation of ternary composites according to different mixing protocols

In this set, effects of different mixing protocols during extrusion on elastomer-glass fiber-recycled PET ternary composites were examined. For this purpose, 20 % elastomer-20 % glass fiber-60 % recycled PET composite was chosen. At this composition, other than our primary mixing protocol, three different mixing protocols were tried. Selected mixing protocols are given in the following Tables 3.20 - 3.22. Required drying was done according to the conditions in Table 3.11. The samples were extruded in the twin screw extruder with the given extrusion parameters in Table 3.18.

Table 3.20 Addition sequence of materials for Mixing Protocol I

Mixing Protocol I	Side Feeder	Main Feeder
1st Extrusion	Glass Fiber	Elastomer
Binary Composite (GF + Elastomer)		
Drying (120 °C, 4 h)		
2nd Extrusion	-----	(Elastomer+GF) + Recycled PET
Ternary Composite		

Table 3.21 Addition sequence of materials Mixing Protocol II

Mixing Protocol II	Side Feeder	Main Feeder
1st Extrusion	Glass Fiber	Recycled PET
Binary Composite (GF + Recycled PET)		
Drying (120 °C, 4 h)		
2nd Extrusion	-----	(GF+Recycled PET) + Elastomer
Ternary Composite		

Table 3.22 Addition sequence of materials for Mixing Protocol III

Mixing Protocol III	Side Feeder	Main Feeder
1st Extrusion	-----	(Elastomer+ Recycled PET)
Binary Blend (Elastomer + Recycled PET)		
Drying (120 °C, 4 h)		
2nd Extrusion	Glass Fiber	(Elastomer+Recycled PET)
Ternary Composite		

The produced composites were then compression molded according to the process parameters given in Table 3.10, after drying. With the proper knives, specimens for characterization experiments were obtained.

3.3 Characterization Experiments

3.3.1 Mechanical Tests

All mechanical tests were performed at room temperature. For each type of composite/blend, average results from seven specimens with standard deviations were reported.

3.3.1.1 Tensile Tests

Tensile tests were performed according to ASTM D638M-91a (Standard Test Method for Tensile Properties of Plastics) by a Lloyd LR 30 K Universal Testing Machine. The shape and the dimensions of the specimens were specified according to Type-I in this standard which are given in Figure 3.13 and Table 3.23 [26]. The crosshead speed was 5 mm/min. After stress versus strain diagrams from the measurements were obtained, tensile strength, tensile modulus and elongation at break values were calculated.

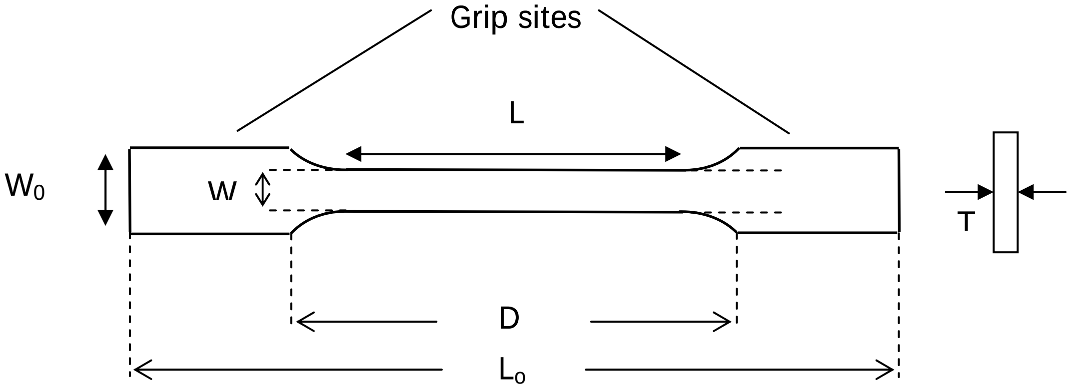


Figure 3.13 Tensile test specimen

Table 3.23 Tensile test specimen dimensions

Dimensions	Specimen Dimensions (mm)
W – width of narrow section	10 ± 0.5
L – length of narrow section	60 ± 0.5
W_0 – width of overall	20 ± 0.5
D – distance between grips	115 ± 5
T – thickness	2.2 - 2.8

3.3.1.2 Flexural Tests

Three-point bending tests were performed according to Test Method-I Procedure A of ASTM D790M-92 (Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics) [41] by a using Lloyd LR 30 K Universal Test Machine. A three-point loading scheme is illustrated below, in Figure 3.14 and the dimensions of the specimens are given in Table 3.24.

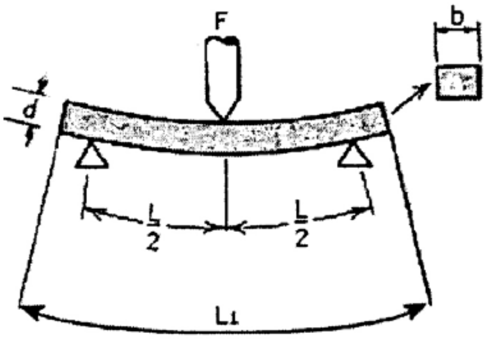


Figure 3.14 A three-point loading scheme [42]

Table 3.24 Flexural test specimen dimensions

Dimensions	Specimen Dimensions (mm)
L_1 (specimen length)	80
B (width of beam tested)	12
D (depth of beam tested)	2.2 – 2.8
L (support span length)	50

3.3.1.3 Impact Tests

Charpy Impact tests were performed by using a Pendulum Impact Tester of Coesfeld Material Test, according to the Test Method-I Procedure A in ASTM D256-91a (Standard Test Method for Impact Resistance of Plastics) [43]. Dimensions of the unnotched samples were 60x12x4 mm, respectively. A schematic drawing of the machine is illustrated in Figure 3.15.

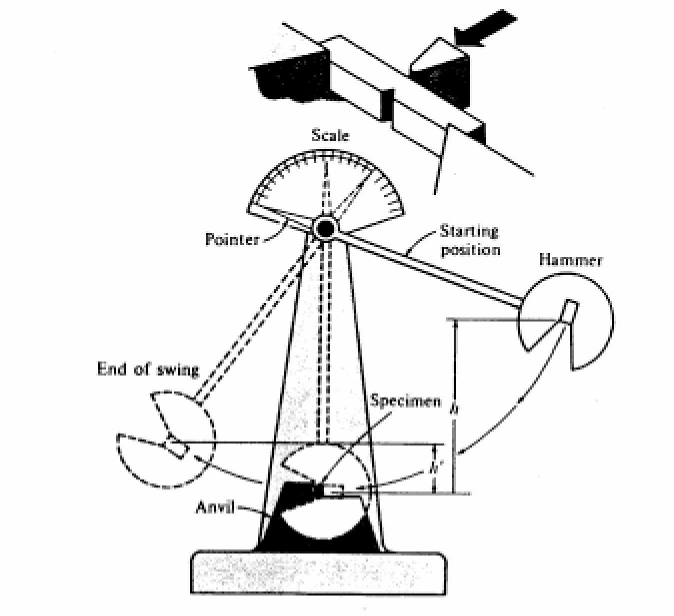


Figure 3.15 Charpy-type impact machine

3.3.2 Morphological Analysis

3.3.2.1 Scanning Electron Microscopy (SEM) Analysis

A low voltage SEM (JEOL JSM-6400) was used to analyze the fractured surfaces from tensile tests as related to the content of elastomer and glass fiber. The fracture surfaces were coated by a sputter coater within a thin layer of gold prior to fractographic examination. The SEM photographs were taken from x400 to x1500 magnification.

3.3.3 Differential Scanning Calorimetry (DSC) Analysis

DSC analyses were carried out from 25 °C to 400 °C with a 20 °C/min heating rate under nitrogen atmosphere by using a differential scanning calorimeter General V 4.1 C Dupont 2000.

3.3.4 Melt Flow Index (MFI) Analysis

Melt flow index (MFI) measurements were carried out according to ASTM D1238-79 using an Omega Melt Flow Indexer. Conditions of temperature and load were selected as 250 °C and 2.16 kg respectively, which were in accordance with material specifications. This method is based on determining the melt index, defined as the mass flow rate of polymer through a specified capillary. Mass flow rate is expressed as grams per 10 minutes. Since melt flow index values are inversely related to the melt viscosity, changes in viscosity values were evaluated for each formulation.

3.3.5 Fiber Length Distribution

For fiber length distribution analysis, approximately 5 g of selected composites from extruded pellets were placed in an oven at 600 °C for 60 minutes to remove the polymeric matrix. The residue, which was glass fiber, was dispersed in distilled water and transferred to the glass slides. The slides were then placed on the optical microscope and the pictures of glass fibers were taken. From each slide approximately ten pictures were obtained for image analysis.

For each sample, a population of about 400 fibers were scaled and counted for fiber length measurements. Fiber lengths were measured with the help of “Sigma Scan$^{®}$” digital image analyzing software.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Mechanical Analysis

4.1.1 Tensile Properties

4.1.1.1 Set I

The tensile strength of extruded pure recycled PET was determined from injection molded specimens. Unlike other sets, in this set injection molding technique was used because in compression molding technique, specimens must be cut from plates formed by compression molding with proper knives, but compression molded recycled PET can not be cut due to its highly brittle behavior. Tensile strength of the recycled PET was determined as 50.4 MPa. This is somewhat lower than virgin PET which was reported as 72 MPa [44] as the processing techniques applied to virgin PET for bottle production, and additives added during bottle production (i.e. UV stabilizers, PVC, etc.) decreases the molecular weight of the PET to some extent. This causes the reduction of mechanical properties of PET.

The tensile modulus (Young Modulus) of extruded recycled PET was determined again from injection molded specimens. Tensile modulus of the recycled PET was determined as 2450 MPa. This is nearly the same as that of virgin PET which was reported as 2750 MPa [44].

The elongation at break of recycled PET was determined as 3.58 %. This is significantly lower than that of virgin PET which was reported as 60 % [44]. This difference may be the result of additives added during the bottle production from virgin PET and also molecular weight reduction of recycled PET.

4.1.1.2 Sets II-III-VI

In these sets, glass fiber-recycled PET composites, elastomer-recycled PET blends and elastomer-glass fiber-recycled PET composites were examined and their tensile strength, tensile modulus and elongation at break values are given in Figures 4.1, 4.2 and 4.4. Tensile results indicate that in glass fiber-recycled PET binary composites, the highest tensile strength is observed at 30 % glass fiber by giving a maximum. Up to 30 % glass fiber, the increase in tensile strength can be based on the increase in weight fraction of glass fiber. Then, the decrease in tensile strength beyond 30 % glass fiber addition may be due to the higher possibility of damaging the fibers as the fiber content increases, since the fiber-fiber interactions increases. When damaged fibers increases, more fibers will be obtained and their lengths will be lower than the critical fiber length and this will cause the decrease in tensile properties. Critical fiber length, L_c is the length of fibers which can be pulled out of the composite without breaking the fiber [45]. When the length of fibers reduces below the critical fiber length, ends of short fibers can not transfer stresses from the matrix to the fiber and fiber ends act as stress concentrators which weaken the material.

Tensile strength of the binary blends of elastomer-recycled PET decreases with increasing elastomer content as expected as due to lower strength of the elastomer. From a mechanical point of view, elastomer acts as voids, reduces the effective matrix area bearing the tensile load.

When the tensile strength of ternary composites are examined, maximum tensile strength is observed at composites containing 10 % elastomer, and with the increase of elastomer content, tensile strength decreases regardless of addition or increase of glass fiber. This designates that the effect of elastomer is more dominant than glass fiber on tensile strength of composites.

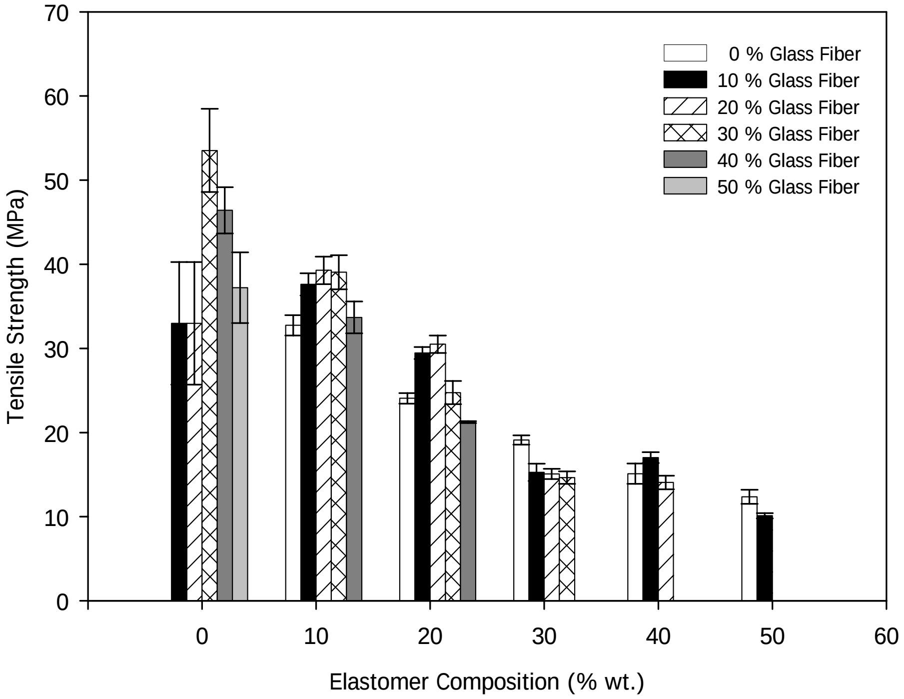


Figure 4.1 Tensile Strength values for binary and ternary systems

It is seen in Figure 4.2 that tensile moduli values of the elastomer-recycled PET blends also have a decreasing trend with the addition of elastomer similar to tensile strength. This result is mainly due to the addition of a rubbery material to the system.

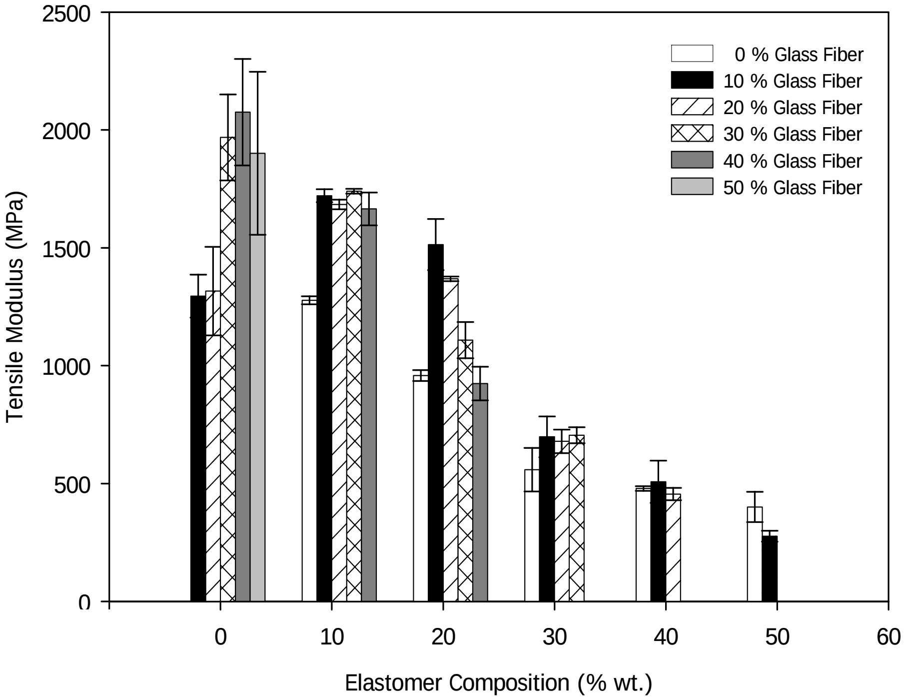


Figure 4.2 Tensile Modulus values for binary and ternary composites

When glass fiber-recycled PET binary composites are considered in the same figure, maximum tensile modulus is observed at 40 % glass fiber containing composites and it is just higher than the tensile modulus of composites with 30 % glass fiber, so there is a similar trend as seen in the tensile strength results. Tensile modulus in ternary composites does not change significantly with the increase in glass fiber content at 10 % elastomer compositions, but when elastomer content increases from 10 % to 50 %, tensile modulus values start to decrease regardless of the increase in glass fiber content. This indicates that elastomeric behavior begins to influence the matrix beyond a certain composition. The high tensile moduli of the ternary composites at 10 % elastomer concentration can be explained according to the reactions occurring in the system. The glycidyl methacrylate group of elastomer may react with the carboxyl and hydroxyl groups of PET as given in Figure 4.3.

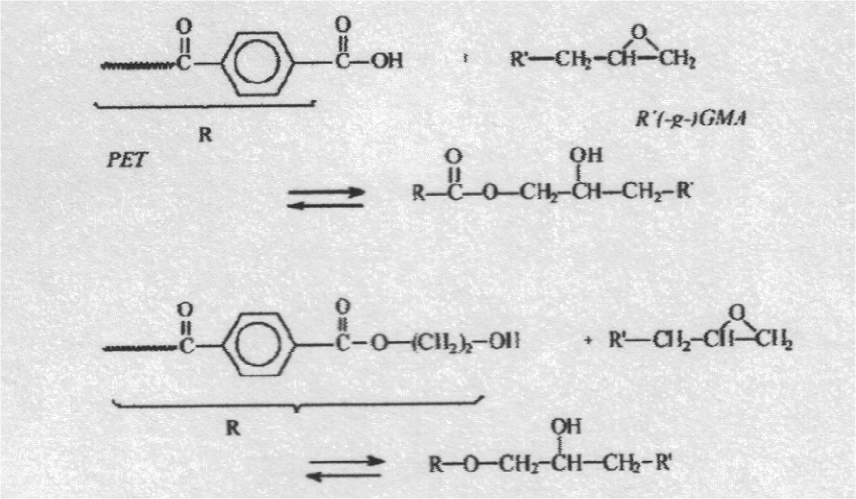


Figure 4.3 Chemical reaction schemes for epoxide and PET functional end groups [46].

Due to higher degree of acidity of the carboxyl group, it is believed that the preferred reaction is the one between the epoxide and the carboxyl functionality. These reactions result in the formation of graft copolymers across the interface [46] that leads to an increase in tensile moduli. Also the impact results which will be given further support this phenomenon. It is also seen that after 20 % of elastomer, for the same elastomer content, tensile modulus decreases with the increase of glass fiber content. This may be the result of fiber length reduction below the critical fiber length due to increase of the viscosity which causes an increase of the shear stress during extrusion with the addition of elastomer. This phenomenon results as a decrease in tensile moduli of the composites with the increase of fiber content.

Elongation at break values of the blends and the composites are represented in Figure 4.4. For elastomer-recycled PET binary system, the elongation at break increases significantly after 10 % elastomer, stays

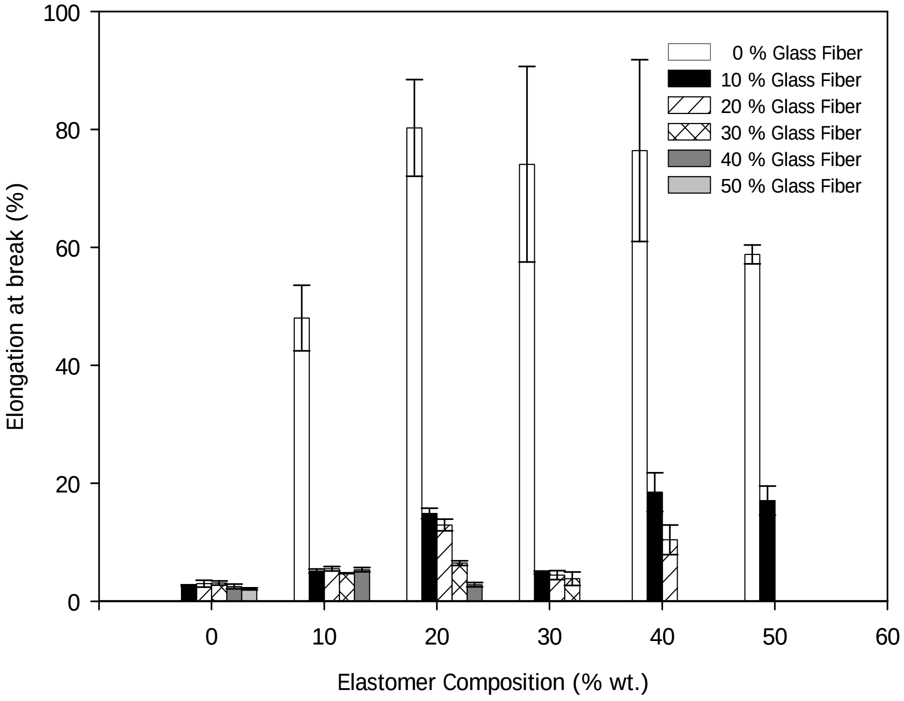


Figure 4.4 Elongation at break values graph for binary and ternary systems

nearly constant at 20-40 % and decreases slightly at 50 % elastomer. This is not surprising since incorporation of rubbery material into the system imparts flexibility and gives high elongation at break values. In addition, the observed trend in the Figure 4.4 may also support that the elastomeric effect starts after a certain composition of elastomer, which was mentioned before. It is seen from the graph that elongation at break values for glass fiber-recycled PET binary system was rather low because of the brittle and rigid behavior of glass fiber-recycled PET system.

Elongation at break values for ternary composites do not show a consistent trend with the increase in glass fiber and elastomer. At 10 % glass fiber content, % elongation at break of the composites increases first up to 20 % elastomer concentration and then decreases with further addition of elastomer. The effects of both glass fiber and elastomer on the elongation at break values compete with each other.

4.1.1.3 Sets IV-V

In these sets, effects of extruder processing parameters on 30 % glass fiber-70 % recycled PET composites and 30 % elastomer-70 % recycled PET blends were examined. As seen in Figures 4.5 and 4.6, there are not significant changes in tensile strength values of the elastomer-recycled PET binary blends with either change of screw speed or extruder temperature profile. In glass fiber-recycled PET system, screw speed of 230 rpm and the temperature profile with 290 °C die temperature profile gives a maxima.

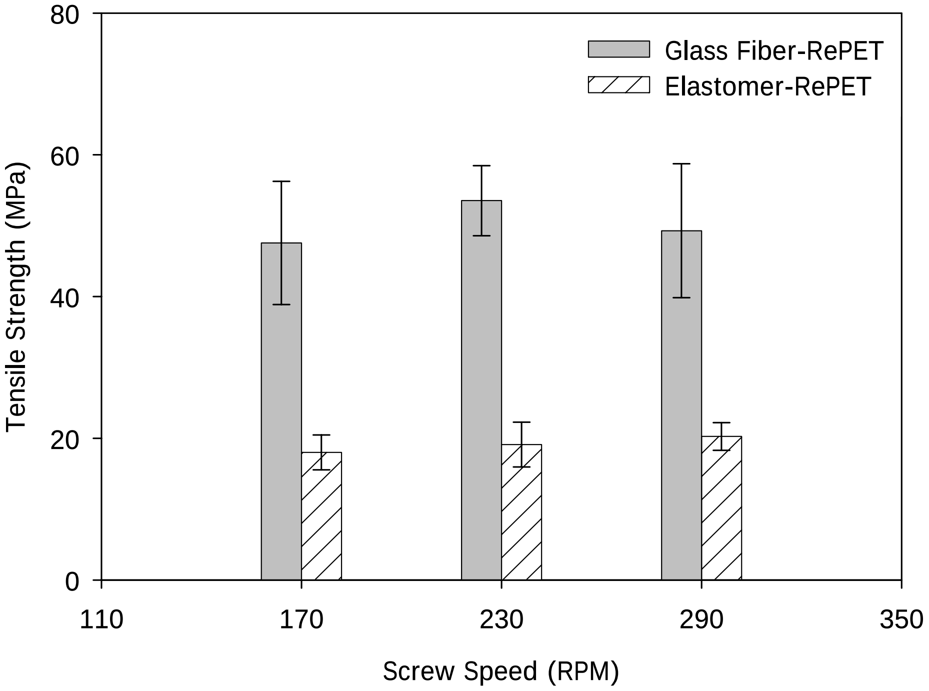


Figure 4.5 Effect of screw speed on tensile strength of binary systems

This may be explained in terms of average fiber length for both cases. At 170 rpm, fibers may remain long and at 290 rpm fibers became too short, that is under critical fiber length and these will affect the tensile strength in a negative way. 230 rpm seems optimum for fiber length distribution which is also shown in the analysis given in Section 4.3. It is clear that temperature profile in extrusion directly affects the melt viscosity during extrusion and degradation of polymers. Viscosity of the melt also has effect on fibers, such that in less viscous melts, fibers will remain longer due to ease of flow, less shear and less probability of collisions during flow.

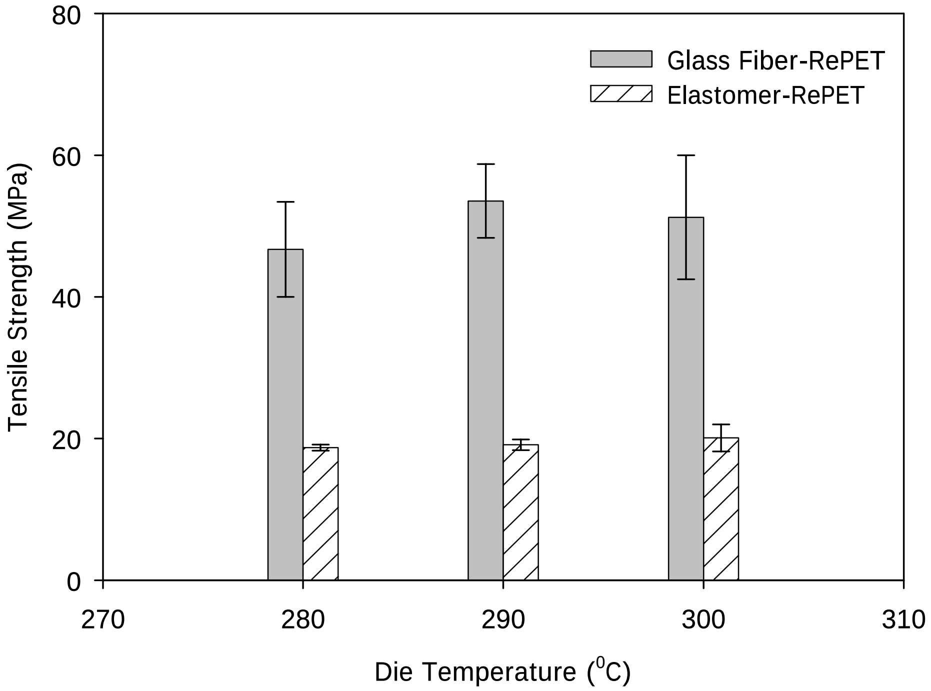


Figure 4.6 Effect of temperature profile on tensile strength of binary systems

At 290 °C die temperature, glass fiber-recycled PET composites have the optimum tensile strength value.

The effects of extrusion parameters on the tensile modulus of the binary systems are shown in Figures 4.7 and 4.8. It is obvious that tensile moduli are not affected considerably in both cases with the change in screw speed and temperature profile.

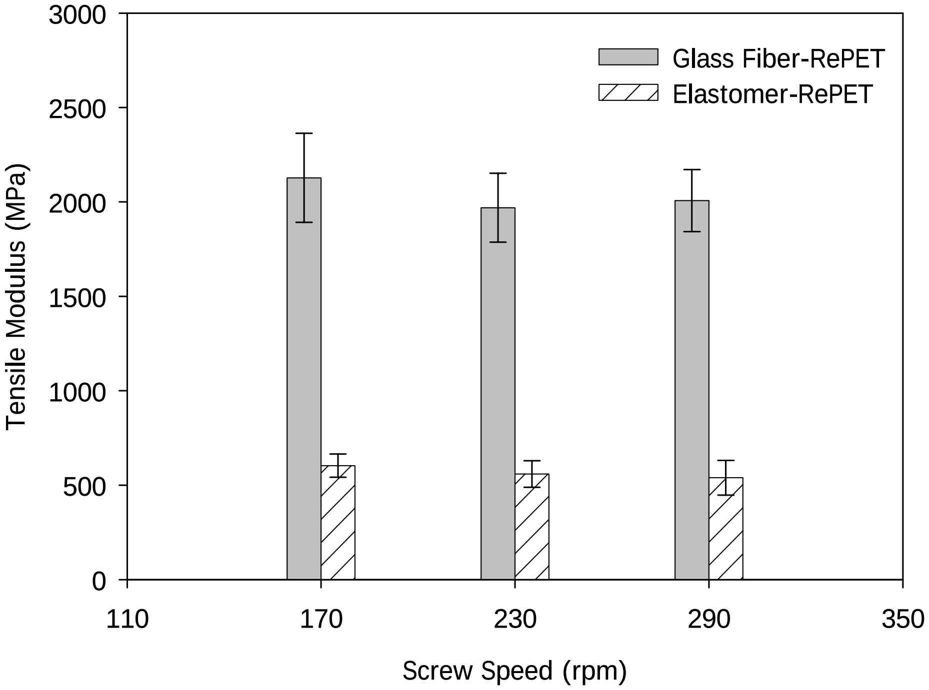


Figure 4.7 Effect of screw speed on tensile modulus of binary systems

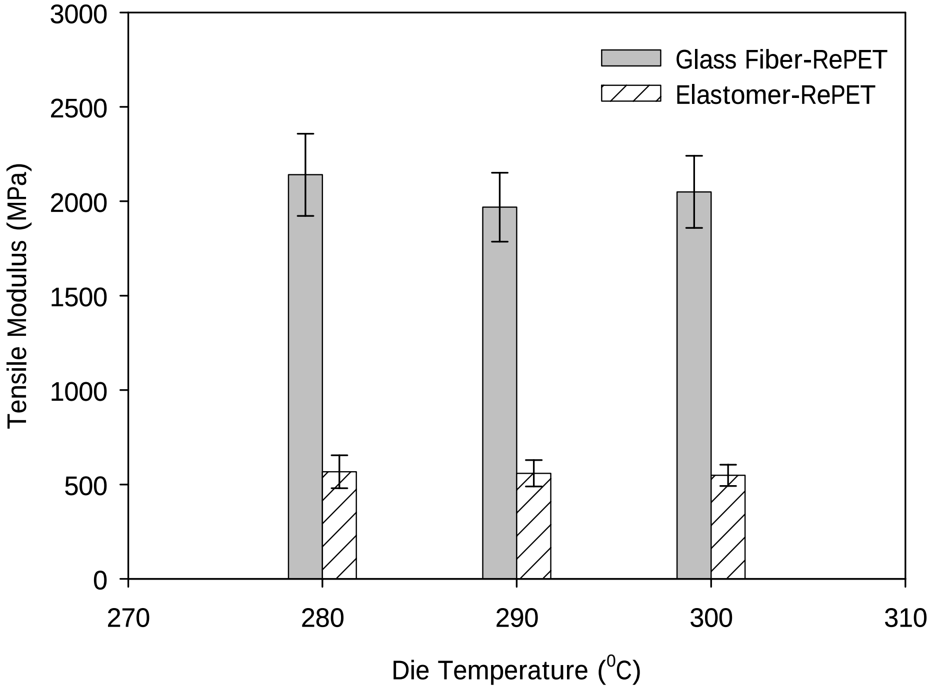


Figure 4.8 Effect of temperature profile on tensile modulus of binary systems

Figure 4.9 shows the effect of screw speed on elongation at break values of elastomer-recycled PET blends. There is an increasing trend in % elongation values with respect to screw speed. This may be due to the increase of shear associate with increase in screw speed. The increase in screw speed, results in higher degree of mixing and dispersion. With the increase of dispersion, voids that convert high unidirectional impact stresses into smaller, harmless multi-directional stresses increase, and this improves not only the elongation at break properties, but also the impact properties of the blend.

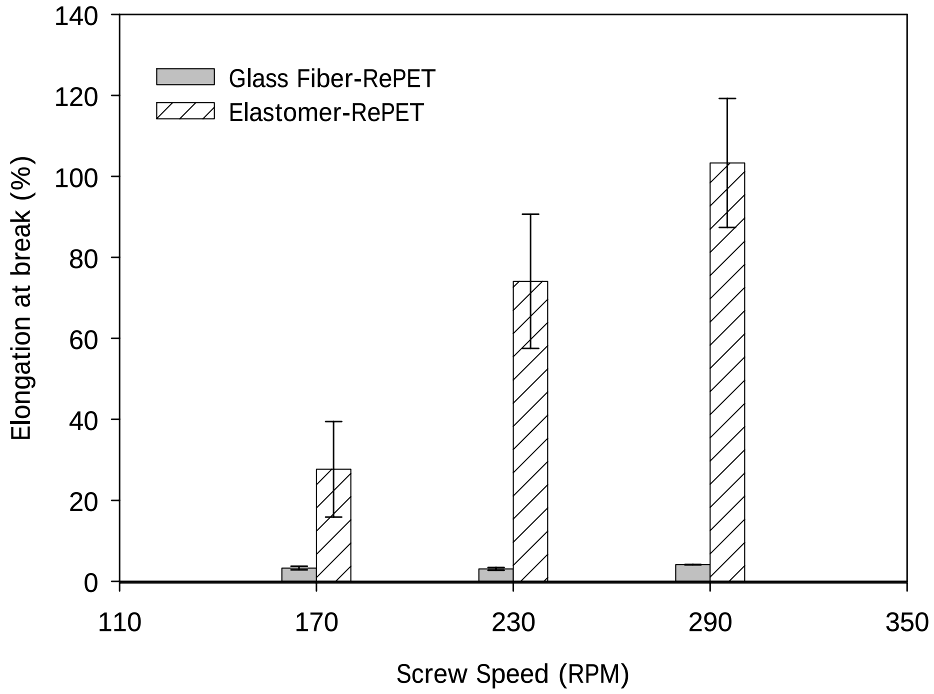


Figure 4.9 Effect of screw speed on elongation at break values of binary systems

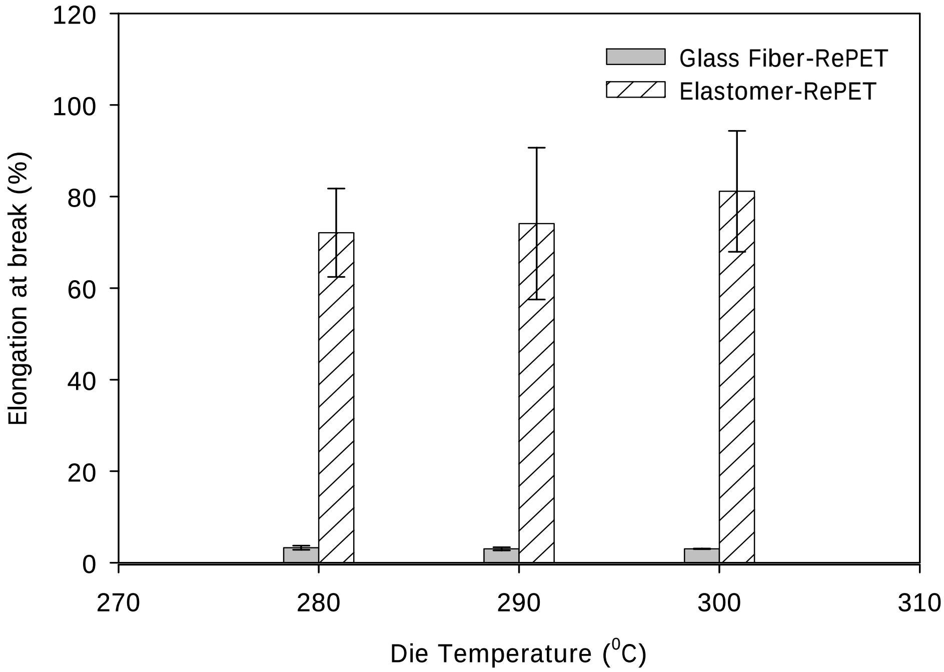


Figure 4.10 Effect of temperature profile on elongation at break values of binary systems

Elongation at break values for both elastomer and glass fiber containing systems are not affected considerably with the changes in processing temperature during extrusion.

4.1.1.4 Set VII

In this set effect of elastomer type on mechanical properties of ternary composites were examined. For this purpose, other than Lotader AX8900, four different types of elastomers were chosen and tried at the

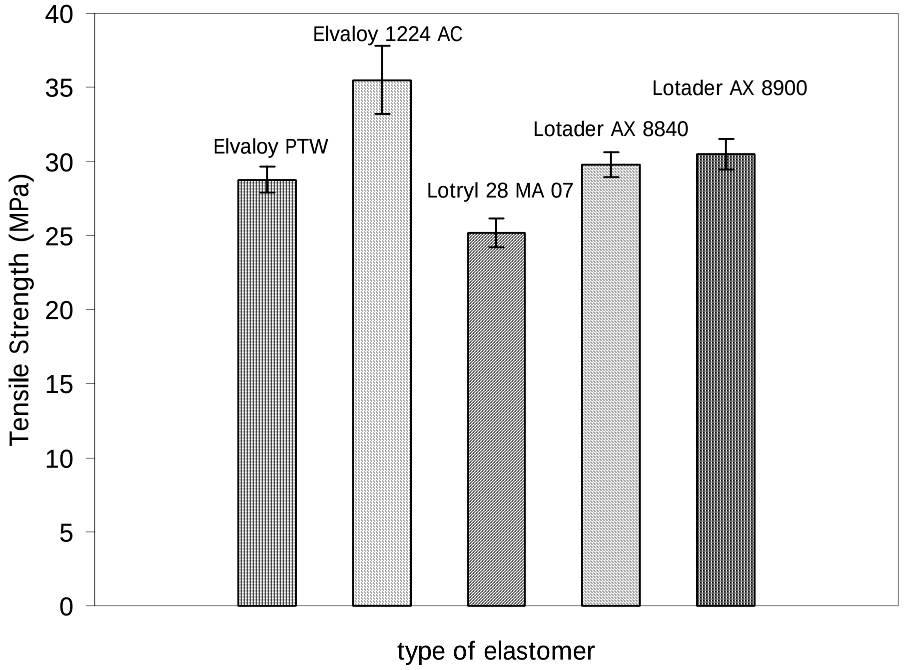


Figure 4.11 Effect of elastomer type on tensile strength of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

composition of 20 % elastomer-20 % glass fiber-60 % recycled PET ternary composites. This composition was chosen because when all the mechanical properties are considered it seems as a reasonable alternative among the others. It is seen in Figure 4.11 that tensile strength of the composite with Elvaloy 1224 AC is somewhat higher than that of other composites followed by Lotader AX8900.

The effect of elastomer type on tensile modulus of selected ternary composite is given in Figure 4.12. Due to lack of GMA functionality and as a result of incompatibility with the matrix, Lotryl 28 MA 07 gave the smallest tensile modulus value. The maximum values of tensile moduli were obtained for composites including Lotader AX8900 and Lotader AX8840. This may be due to the possible reactions between the functional groups of elastomer and PET, but this reason is also valid for other functional elastomers used. The extent of the reactions occurring in the system is questionable.

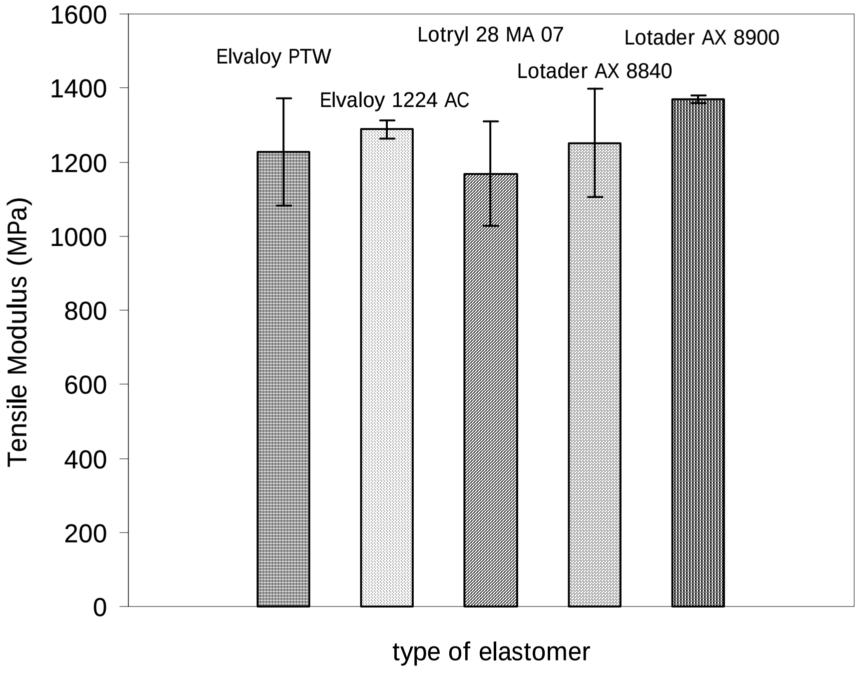


Figure 4.12 Effect of elastomer type on tensile modulus of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

Figure 4.13 represents the effect of elastomer type on % elongation at break values of selected ternary composite. The highest elongation at break value is observed for the composite including Lotader AX8900.

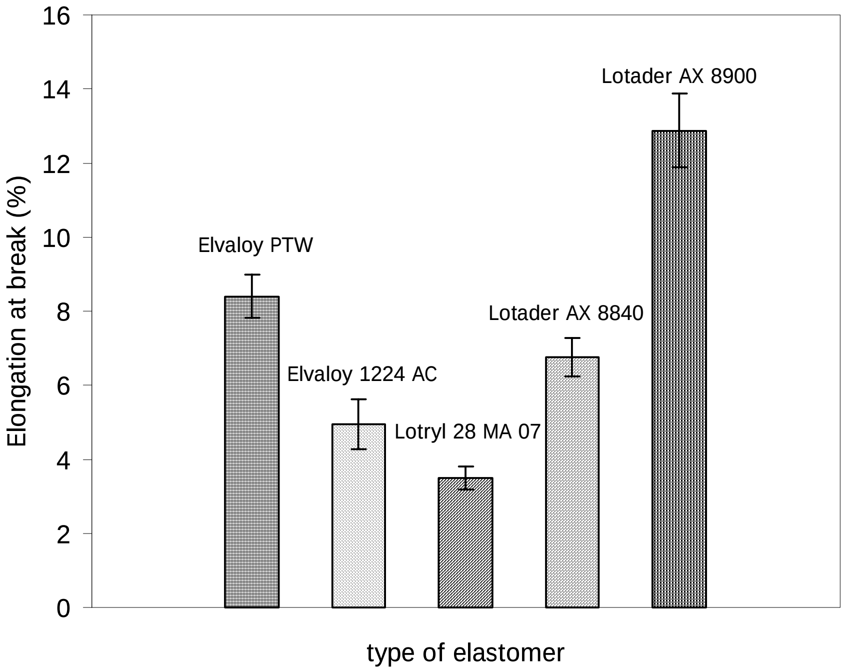


Figure 4.13 Effect of elastomer type on elongation at break values of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

4.1.1.5 Set VIII

In this set, effect of mixing sequences on mechanical properties of ternary composites was examined. Again these experiments were done for the 20 % elastomer-20 % glass fiber-60 % recycled PET composition. Three different mixing protocols, which were explained in the experimental section, were tried differing from the original mixing protocol. In original protocol, elastomer and recycled PET were fed together from the main feeder and glass fiber from the side feeder. In mixing protocol 1, first glass fiber and elastomer were extruded and then this composite was extruded with recycled PET. In mixing protocol 2, firstly glass fiber and recycled PET were extruded and then this composite was extruded with elastomer. In mixing protocol 3, firstly elastomer and recycled PET were extruded and then this blend was extruded with glass fiber.

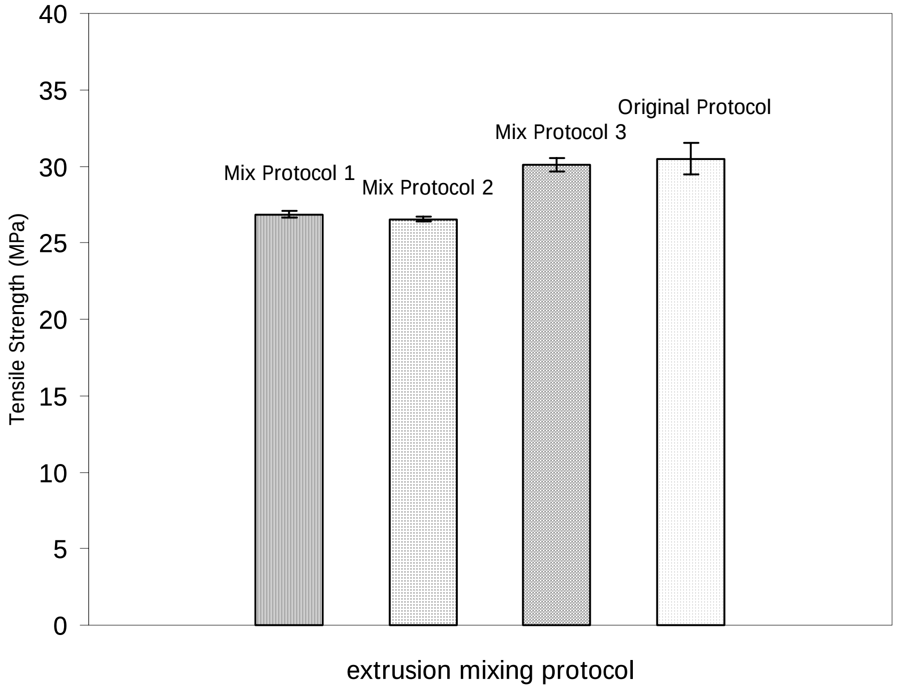


Figure 4.14 Effect of mixing protocol on tensile strength of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

Figure 4.14 shows that tensile strength values decrease in other tried protocols. This may be a result of double extrusion process used in mixing protocols 1, 2 and 3. As the extrusion cycles increases, molecular weight of the PET decreases due to the degradation in the system [47] which decreases the mechanical properties of the composites. Also, the fiber length decreases if fibers undergo two extrusion steps.

Effect of mixing protocol on tensile modulus of selected ternary composite is in a similar trend with the tensile strength. The significant difference is in the original mixing protocol, unlike tensile strength, the minimum tensile modulus was observed at this protocol, which was unexpected.

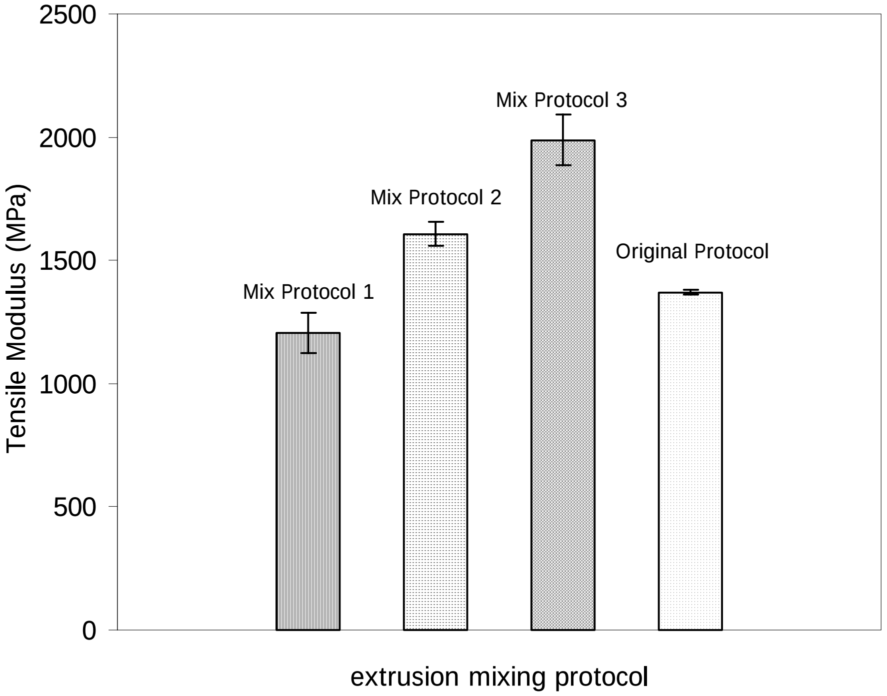


Figure 4.15 Effect of mixing protocol on tensile modulus of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

Figure 4.16 shows the elongation at break values for different mixing protocols of the selected composite. The highest value was achieved at original mixing protocol. This may be due to the application of double extrusion in mixing protocols 1, 2, and 3 which may cause degradation of PET and low elongation at break values.

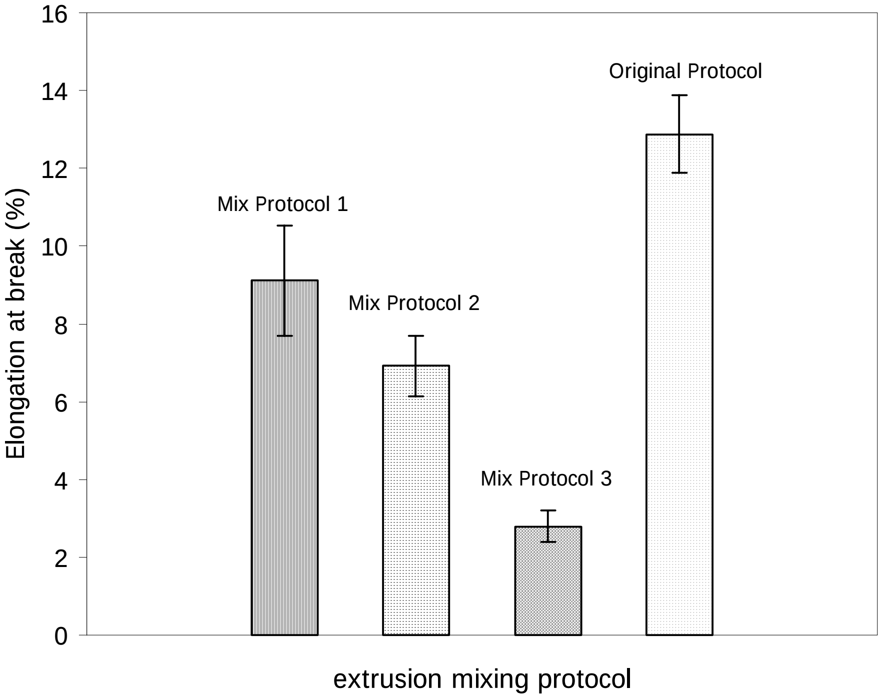


Figure 4.16 Effect of mixing protocol on elongation at break values of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

4.1.2 Flexural Properties

4.1.2.1 Set I

Flexural strength and flexural modulus of extruded pure recycled PET were determined as 71.40 MPa and 2680.30 MPa, respectively.

4.1.2.2 Set II-III-VI

It is seen in Figure 4.17 that flexural strength values are in similar trend with the tensile strength values of both binary and ternary systems.

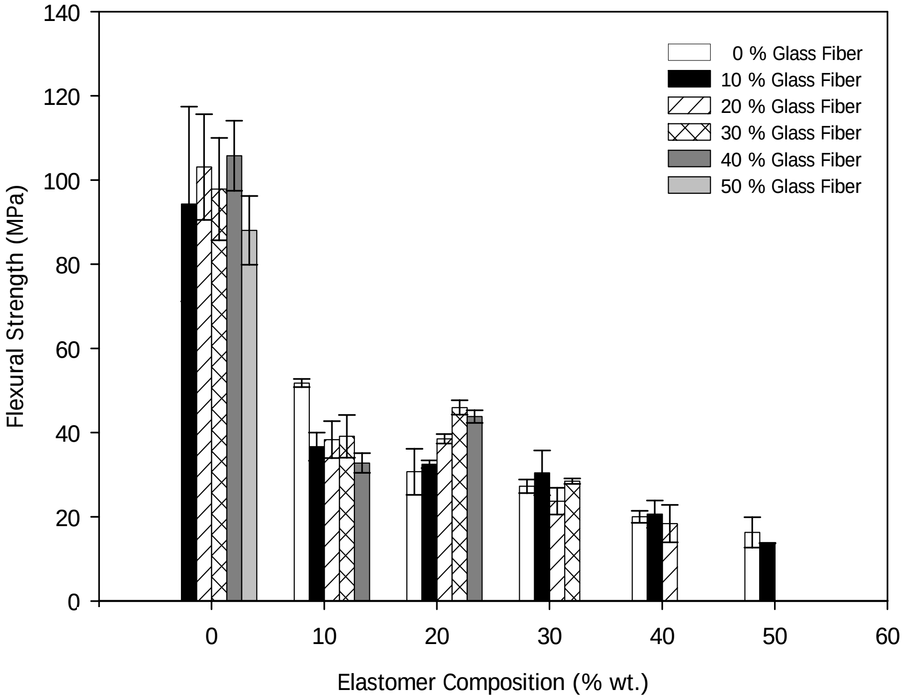


Figure 4.17 Flexural Strength values for binary and ternary systems

Flexural moduli of the binary and ternary systems are given in Figure 4.18. It is seen that flexural modulus of the glass fiber-recycled PET binary system increases with increasing glass fiber content since glass fiber has higher modulus, and addition of a high modulus compound leads to an improvement in the stiffness of the polymer. From the similar point of view, flexural modulus of the elastomer-recycled PET binary system decreases with the addition of elastomer having low modulus. Ternary composites,

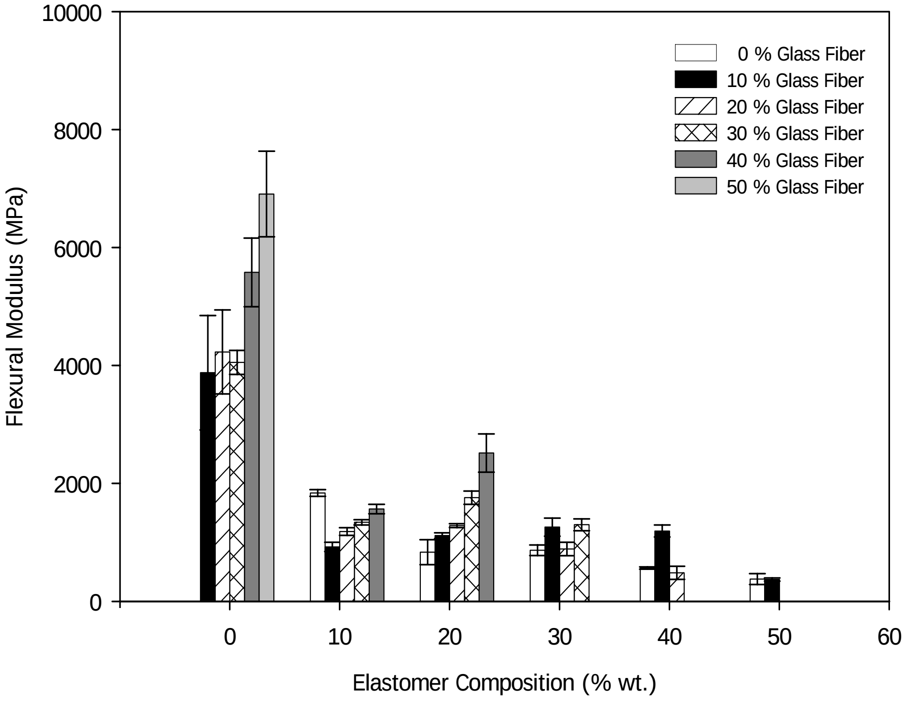


Figure 4.18 Flexural Modulus values of ternary and binary systems

containing 20 % elastomer have the highest flexural moduli values than the others. At this composition, flexural modulus of the composites increases with the addition of glass fiber due to high modulus of glass fiber which has much more dominant effect than the expected decrease in average fiber length at high glass fiber content. Further addition of elastomer beyond 20 % results in a decrease in flexural modulus, indicating that rubbery effect of elastomer becomes more dominant.

4.1.2.3 Set IV-V

Figures 4.19 and 4.20 show that flexural strength values of the binary systems are not affected from the extrusion process parameters such as screw speed and processing temperature.

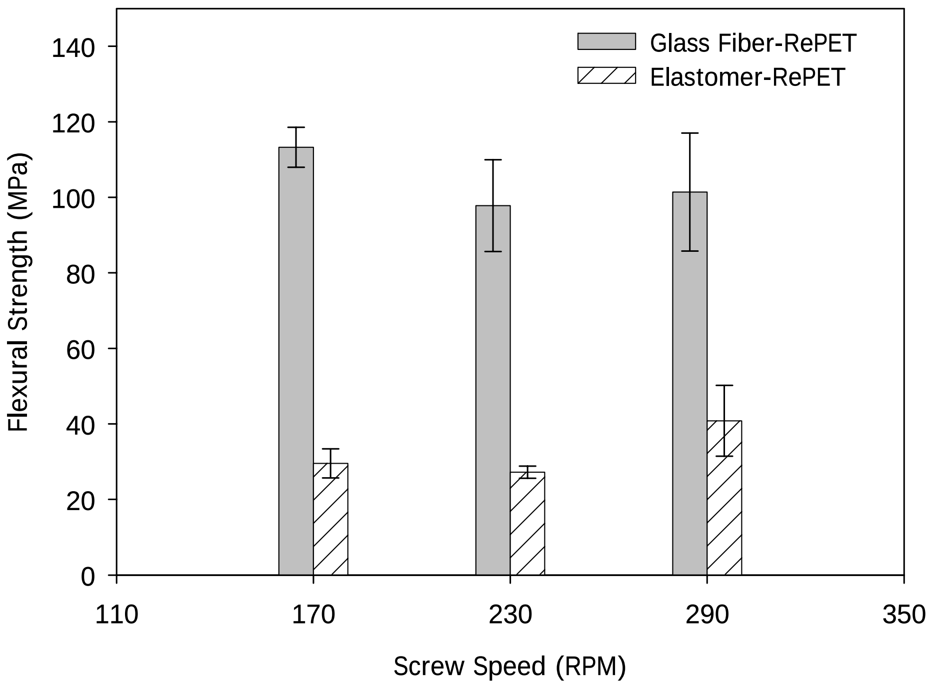


Figure 4.19 Effect of screw speed on flexural strength of binary systems

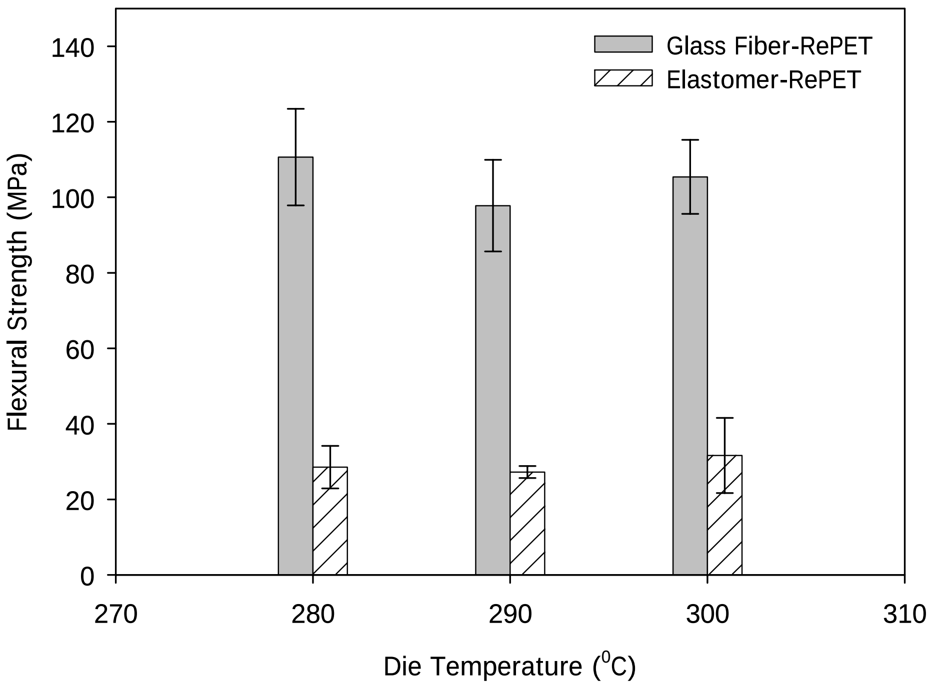


Figure 4.20 Effect of temperature profile on flexural strength of binary systems

It was seen from Figures 4.21 and 4.22 that the changes in screw speed and temperature profile do not affect the flexural moduli of the binary systems.

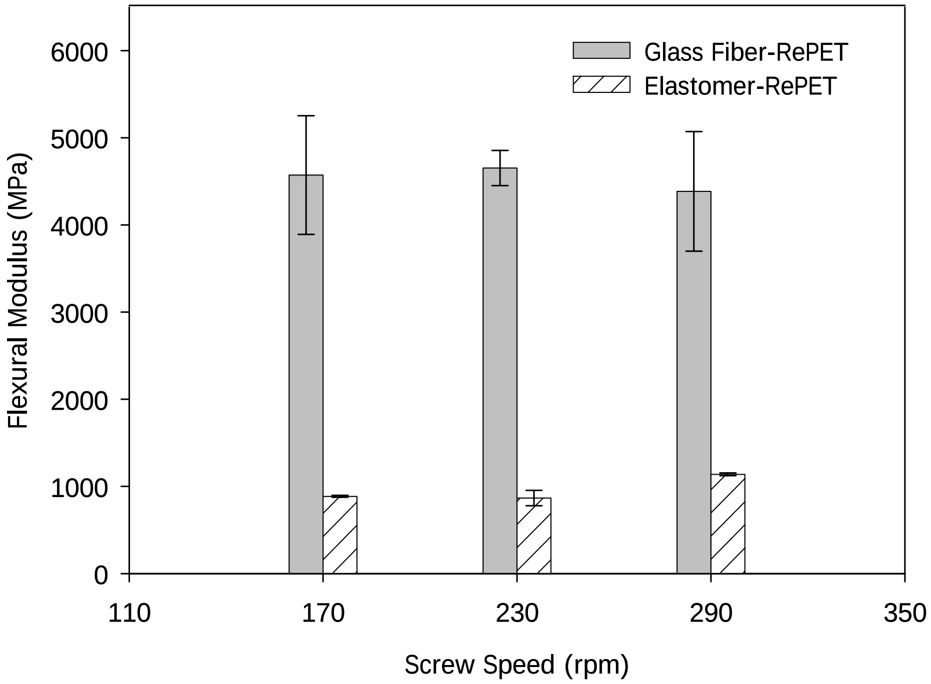


Figure 4.21 Effect of screw speed on flexural modulus of binary systems

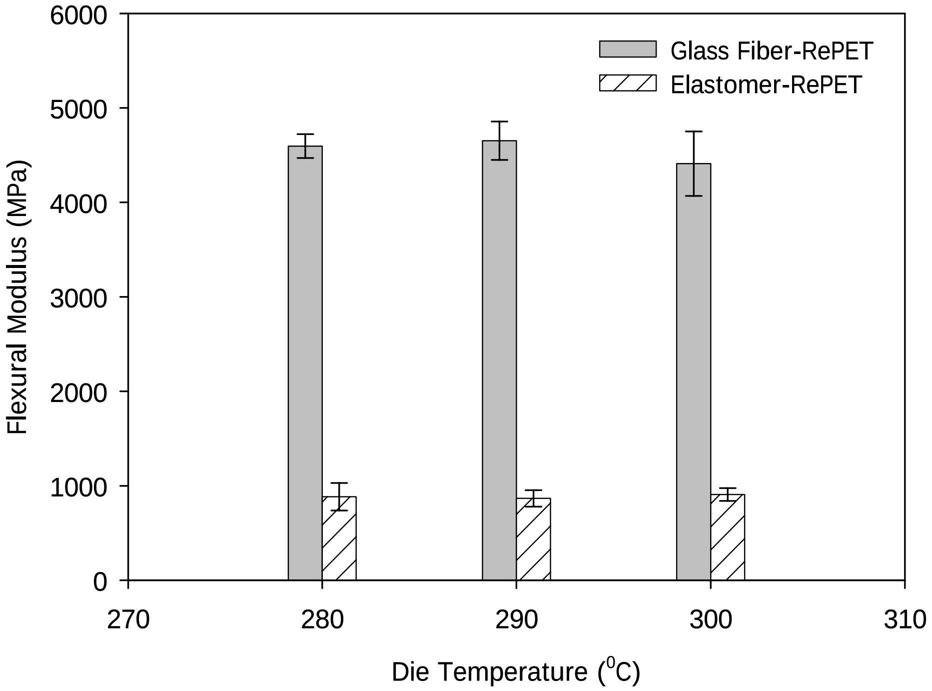


Figure 4.22 Effect of temperature profile on flexural modulus of binary systems

4.1.2.4 Set VII

It was observed from Figure 4.23 that the lowest flexural strength values as observed for composite including Lotader AX8900. This indicates the lower resistance of this type of elastomer to bending.

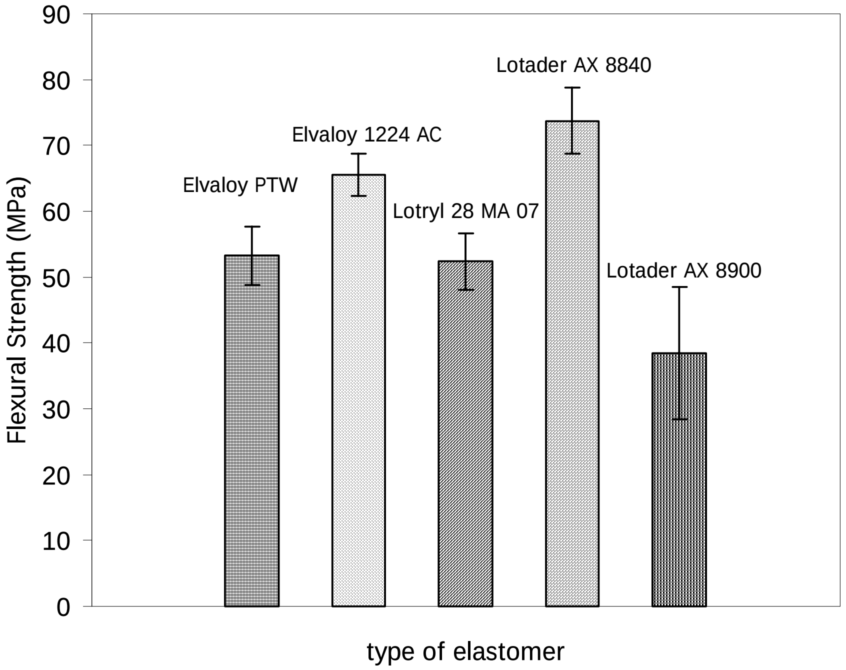


Figure 4.23 Effect of elastomer type on flexural strength of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

It is clear from Figure 4.24 that the highest flexural modulus data was obtained by using Lotader AX8840 type elastomer in selected ternary composite. This may be a result of a graft copolymer formation to a certain extent between functional groups of elastomer and PET.

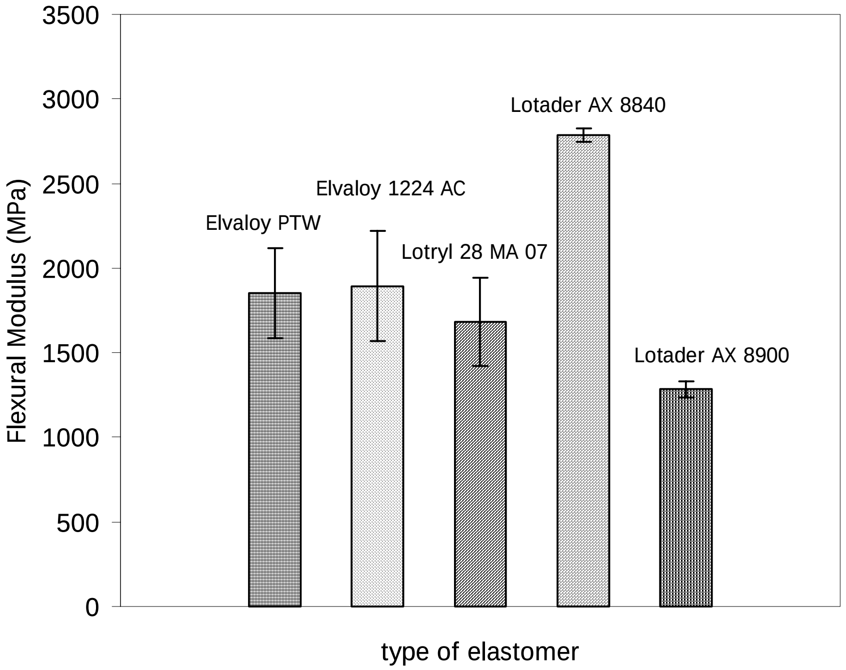


Figure 4.24 Effect of elastomer type on flexural modulus of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

4.1.2.5 Set VIII

The original mixing protocol gave the lowest flexural strength value that indicates also the lowest resistance to bending. This is somewhat unexpected since original sequence of addition involves one step extrusion in which possibility of degradation is less on the contrary the other sequences involve a two step extrusion, which should cause decrease in mechanical properties due to the decrease in molecular weight upon degradation.

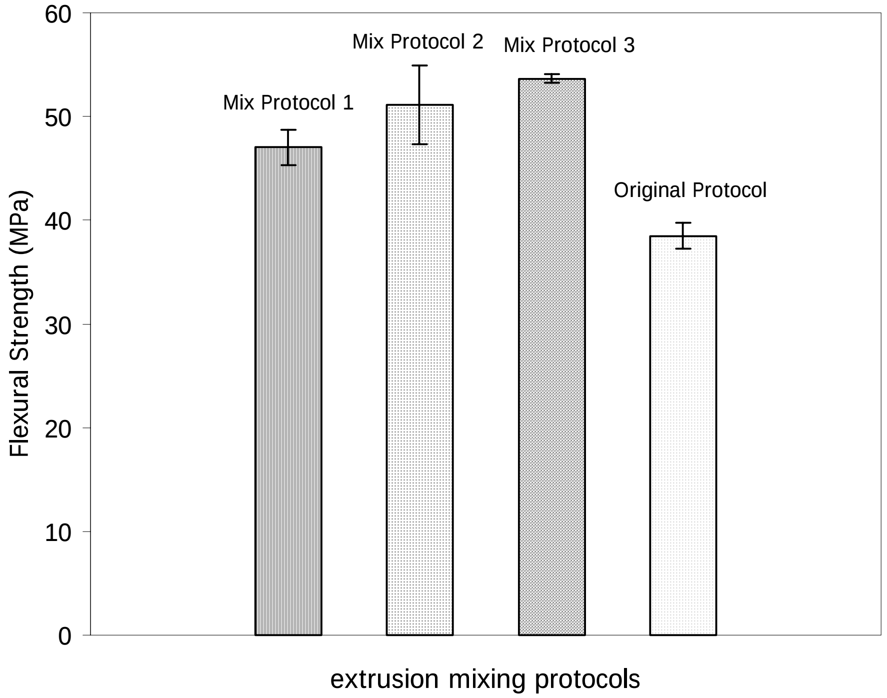


Figure 4.25 Effect of mixing protocol on flexural strength of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

When mixing protocols used during experiments are compared to analyze flexural modulus of the composites, it is seen that mixing protocol 3 gives the best result among the others. This may be the result of the nature of the mixing protocol. In protocol 3, recycled PET and elastomer was first blended in the first step, and the glass fiber was added to the preblended system, so glass fiber is extruded once and fibers might not be damaged as much as the other protocols and these less damaged and reduced size fibers give more stiffness to the system.

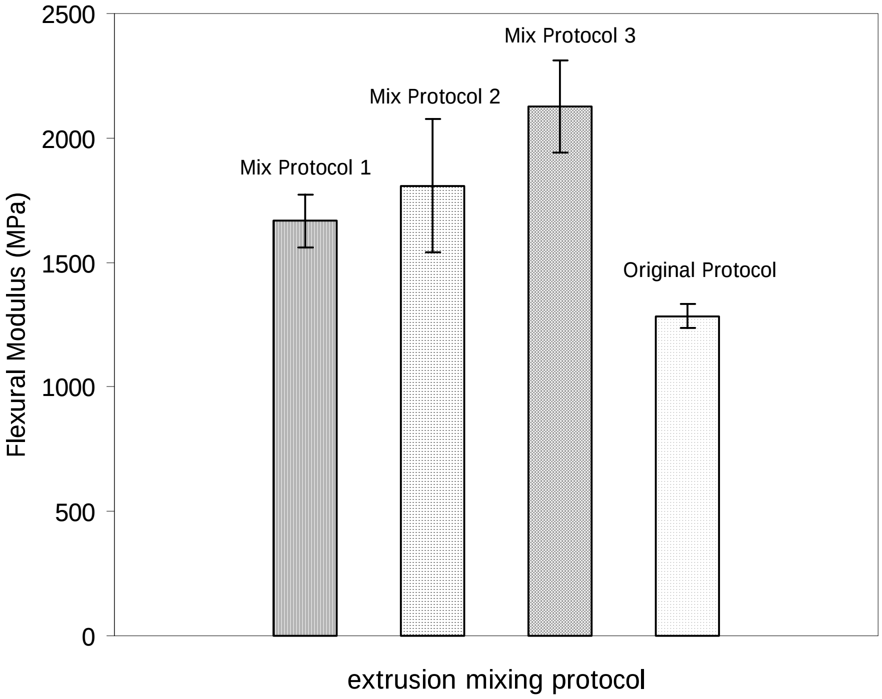


Figure 4.26 Effect of mixing protocol on flexural modulus of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

4.1.3 Impact Properties

4.1.3.1 Set I

For determination of the impact properties of the samples, unnotched Charpy Method was used. Impact strength of the virgin and recycled PET was determined as 19.51 kJ/m^2 and 17.8 kJ/m^2, respectively.

4.1.3.2 Set II-III-VI

Impact modification of PET is very important as PET is very weak to cracks at room temperature due to its brittle structure and these cracks reduce the impact strength when a sudden impact is applied to PET. In order to increase the impact properties of PET, especially the recycled PET, an elastomer which is usually a terpolymer of ethylene, is added to the system.

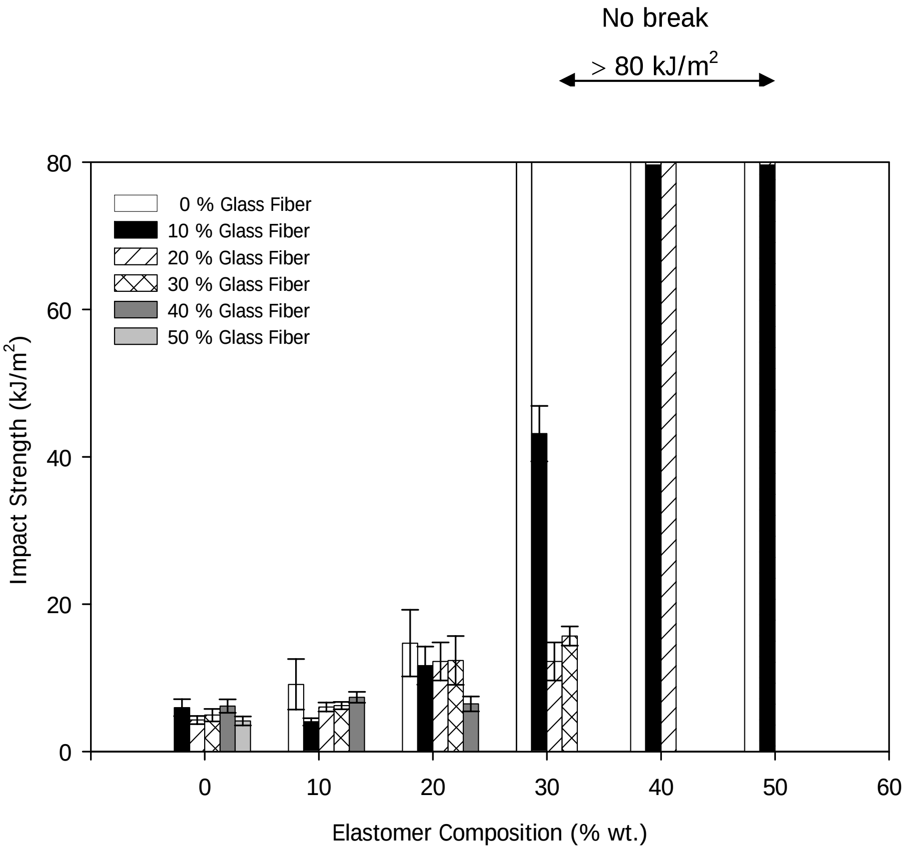


Figure 4.27 Impact Strength values for binary and ternary systems

Composites including only glass fiber show lower impact strength than neat recycled PET (Figure 4.27). This indicates that the incorporation of SGF has restricted the plastic deformation of the matrix. As a result of micromechanical constraints imposed by the fibers, energy absorbed during impact is readily reduced. As seen in Figure 4.27, impact strength of the elastomer-recycled PET blends increases with increasing amount of elastomer. Especially there is a sharp increase starting from 30 % elastomer where the samples were not broken which indicates that impact strength of the blends is higher than 80 kJ/m^2 which is the maximum impact strength that can be measured by the impact tester for this geometry. The impact strength of the glass fiber-recycled PET composites is relatively smaller than that of binary blends including elastomer. In ternary composites, impact strength increases significantly starting from 40 % elastomer composition. Between 10 and 30 % elastomer concentrations, the impact strength values of the ternary system are near or just above the values of the elastomer-recycled PET blends. The main advantage of the ternary system compared to other composites or blends is to use combined effects of both the glass fiber and elastomer in the system without sacrificing the structural properties. Composites with 20 % elastomer show a maximum at 20 % elastomer-20 % glass fiber-60 % recycled PET combination. The decrease in impact strength with the addition of glass fiber at constant elastomer content may be the result of weak dispersion of elastomer particles and/or some reactions occurred in the system that blocks the effect of elastomer by inhibiting the functional groups of the elastomer.

4.1.3.3 Set IV-V

The effect of extrusion process parameters on impact strength of binary composites are shown in Figures 4.28 and 4.29. Impact strength of the binary composites is not affected by these conditions and this is also valid for the blends. Blends’ impact strength could not be measured precisely since no break is observed for both notched and unnotched impact test samples.

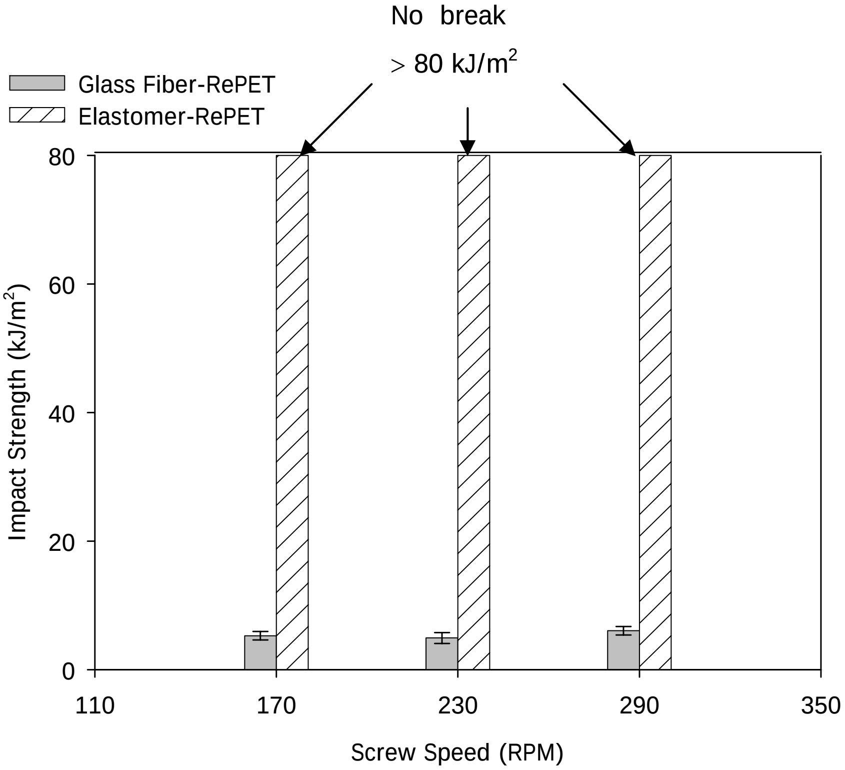


Figure 4.28 Effect of screw speed on impact strength of binary systems

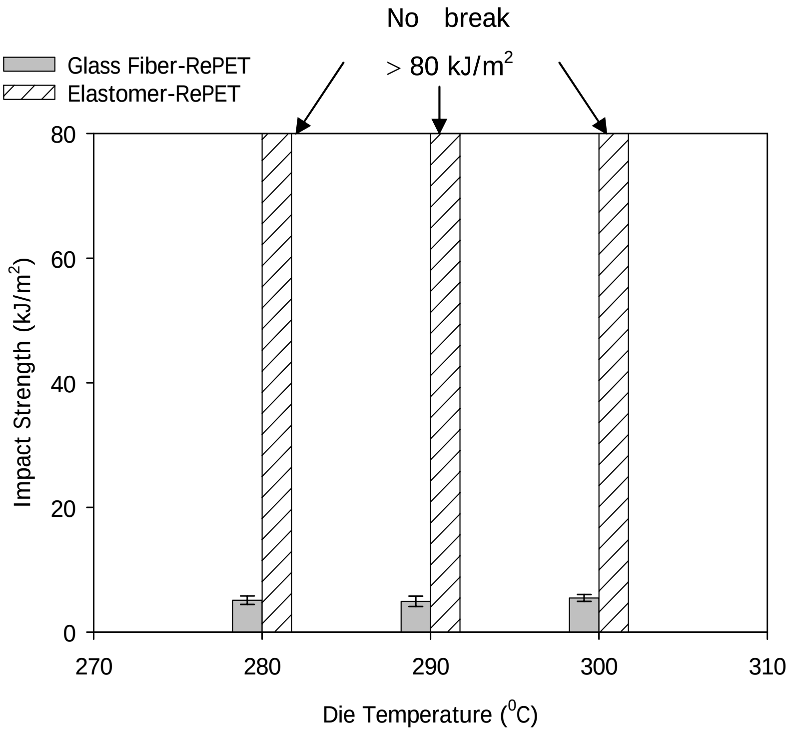


Figure 4.29 Effect of temperature profile on impact strength of binary systems

4.1.3.4 Set VII

The effect of elastomer type on impact strength of selected ternary composite is shown in Figure 4.30. Elvaloy PTW type gives the highest impact strength among the other elastomers by doubling the impact strength when compared with Lotader AX8900. Even though both elastomers have the GMA functionality, Elvaloy PTW includes n-butyl acrylate instead of methyl methacrylate, and somehow it is more compatible with PET matrix or dispersed more efficiently in the matrix.

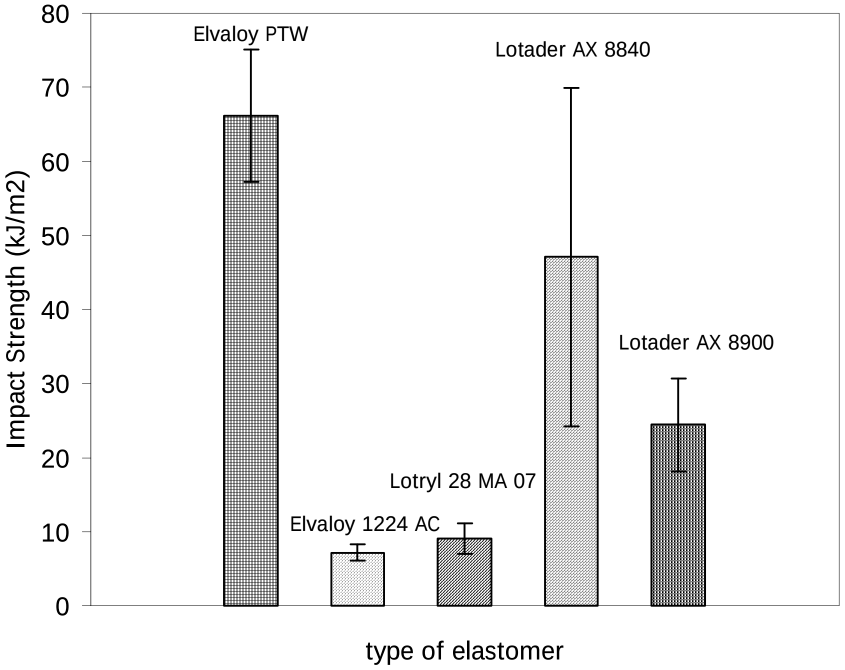


Figure 4.30 Effect of elastomer type on impact strength of ternary composites (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

4.1.3.5 Set VIII

It is seen in Figure 4.31 that the impact strength of the original mixing protocol is the highest among the other protocols. This might be the result of one step extrusion and less degradation occurring in the system. In other protocols, degree of degradation increases with the two step extrusion cycle.

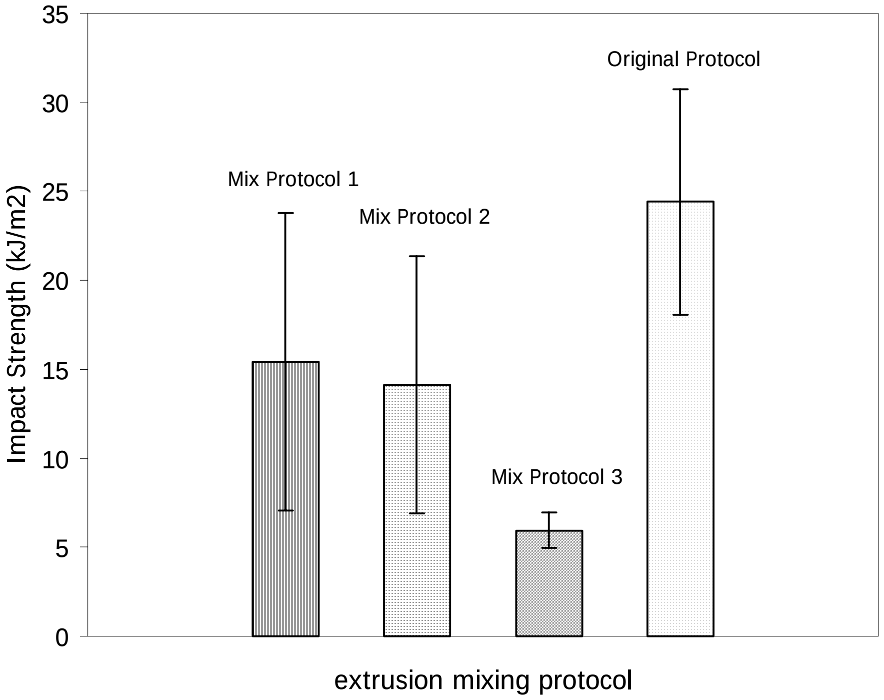


Figure 4.31 Effect of mixing protocol on impact strength of ternary systems (at 20 % elastomer-20 % glass fiber-60 % recycled PET composition)

4.2 Melt Flow Index (MFI) Analyses

Melt flow index measurements were carried out under a specified load of 2.16 kg and at a temperature of 250 °C. As is known, melt flow index is inversely related to the melt viscosity. Besides, the melt viscosity is related to the molecular weight of the material. Melt flow index values of the composites and blends are given in the Tables 4.1 - 4.7. The average of seven data is taken and their standard deviations are given in the tables.

When the results of the MFI analyses are examined, the following points are designated:

As seen in Table 4.1, with the increase of glass fiber content in glass fiber-recycled PET composites, MFI value decreases as the viscosity of the composites increases. In the same manner, Table 4.2 shows that increase of elastomer in elastomer-recycled PET blends decreases MFI values as a result of the increase in viscosity of the blends due to some potential reactions between the blend components.

Tables 4.3 and 4.4 show that, MFI values increase with screw speed, but decrease with the increase of processing temperature during extrusion of glass fiber-recycled PET composites. This indicates that as screw speed increases molecular weight decreases due to the chain scission occurring in the system. When temperature is increased, the possibility of certain crosslinking reactions also increases. Thus, an increase in viscosity is obtained for the binary composites.

Viscosities of elastomer-recycled PET blends give maxima at 230 rpm and at 290 °C die temperature, as seen in Tables 4.5 and 4.6. This may be as a result of the relatively higher degree of crosslinking reactions occurring at these conditions and they increase the viscosity of the melt.

Also it is expected that with the increase of screw speed, residence time in extrusion will be decreased and this will lowers the reactions in the system. As a result, molecular weight of the blends/composites will not increase at high screw speeds, and MFI values will increase. Increase in temperature profile, will cause more reactions in the system and this will increase the molecular weight of the blends/composites which will decrease the MFI values.

When ternary systems are considered, MFI values decrease with increasing elastomer content, as expected due to potential reactions occurring between PET and GMA, and also side reactions between amine groups of glass fiber and GMA, thus viscosity increases. When elastomer concentration is kept constant separately at 20, 30 and 40 %, a decreasing trend in melt flow index (i.e. increase in viscosity) is observed with respect to increasing amount of glass fiber, but this observation is somewhat not valid for the ternary composites containing 10 % elastomer.

Table 4.1 Melt Flow Index Analysis for SGF-re-PET composites

Composite	Melt Flow Index (g/ 10 min)	Stand. Dev.
10 % SGF – 90 % re-PET	116.6	0.8
20 % SGF – 80 % re-PET	97.8	8.4
30 % SGF – 70 % re-PET	26.9	2.3
40 % SGF – 60 % re-PET	22.6	3.4
50 % SGF – 50 % re-PET	13.8	4.9

Table 4.2 Melt Flow Index Analysis for elastomer-re-PET blends

Blend	Melt Flow Index (g/ 10 min)	Stand. Dev.
10 % elastomer – 90 % re-PET	2.9	0.1
20 % elastomer – 80 % re-PET	1.1	0.1
30 % elastomer – 70 % re-PET	0.8	0.2
40 % elastomer – 60 % re-PET	5.9	0.7
50 % elastomer – 50 % re-PET	2.2	0.2

Table 4.3 Effect of screw speed on melt flow of SGF-re-PET composites

Composite	Melt Flow Index (g/ 10 min)	Stand. Dev.
30 % SGF – 70 % re-PET 170 rpm	61.0	2.2
30 % SGF – 70 % re-PET 230 rpm	26.9	2.3
30 % SGF – 70 % re-PET 290 rpm	116.8	2.2

Table 4.4 Effect of temperature profile on melt flow of SGF-re-PET composites

Composite	Melt Flow Index (g/ 10 min)	Stand. Dev.
30 % SGF – 70 % re-PET 280 °C Die Temperature	65.8	9.0
30 % SGF – 70 % re-PET 290 °C Die Temperature	26.9	2.3
30 % SGF – 70 % re-PET 300 °C Die Temperature	14.8	4.6

Table 4.5 Effect of screw speed on melt flow of elastomer-re-PET blends

Blend	Melt Flow Index (g/ 10 min)	Stand. Dev.
30 % elastomer – 70 % re-PET 170 rpm	4.6	1.2
30 % elastomer – 70 % re-PET 230 rpm	0.8	0.2
30 % elastomer – 70 % re-PET 290 rpm	2.3	0.4

Table 4.6 Effect of temperature profile on melt flow of elastomer-re-PET blends

Blend	Melt Flow Index (g/ 10 min)	Stand. Dev.
30 % elastomer – 70 % re-PET 280 °C Die Temperature	2.3	0.3
30 % elastomer – 70 % re-PET 290 °C Die Temperature	0.8	0.2
30 % elastomer – 70 % re-PET 300 °C Die Temperature	1.6	0.6

Table 4.7 Melt Flow Behavior of ternary composites

Composite			Melt Flow Index (g/ 10 min)	Stand. Dev.
Elastomer (%)	SGF (%)	Re-PET (%)		
10	10	80	61.6	4.3
10	20	70	63.9	8.2
10	30	60	68.8	5.5
10	40	50	72.3	2.2
20	10	70	19.5	0.9
20	20	60	16.6	2.0
20	30	50	2.8	0.2
20	40	40	6.7	1.0
30	10	60	12.3	0.8
30	20	50	7.6	0.2
30	30	40	3.4	0.4
40	10	50	2.3	0.2
40	20	40	1.2	0.4
50	10	40	0.4	0.1

4.3 Fiber Length Distribution

Fiber length distributions for certain samples were determined to see the effects of glass fiber content, elastomer content, screw speed and processing temperature on the mechanical properties of composites. Table 4.8 and Figures 4.32 - 4.34 show the fiber length distributions for the different samples that were studied.

As glass fiber content in the composites increases, number average fiber length decreases at constant elastomer content. When elastomer concentration is increased at constant glass fiber content, number average fiber length again decreases due to the shearing effects of high viscosity of elastomer at high elastomer contents.

Table 4.8 Number average fiber length distribution for selected samples

Sample	Number Average Fiber Length (μm)
10 % elastomer – 10 % SGF – 80 % re-PET	359
10 % elastomer – 40 % SGF – 50 % re-PET	308
20 % elastomer – 10 % SGF – 70 % re-PET	383
50 % elastomer – 10 % SGF – 70 % re-PET	341
30 % SGF – 70 % re-PET 170 rpm	353
30 % SGF – 70 % re-PET 230 rpm	402
30 % SGF – 70 % re-PET 290 rpm	319
30 % SGF – 70 % re-PET 280 °C Die Temp.	314
30 % SGF – 70 % re-PET 290 °C Die Temp.	402
30 % SGF – 70 % re-PET 300 °C Die Temp.	422

The critical length of the glass fiber/recycled PET system can be calculated by utilizing the following relationship [45]:

$$\left(\frac{l}{d}\right)_c = \frac{\sigma_{uf}}{2\tau_u} \qquad (4.1)$$

where σ_{uf} is the ultimate fiber strength, τ_u is the fiber-matrix interfacial shear strength. Assuming that the fibers are perfectly bonded, the interfacial shear strength becomes the shear strength of the polymer matrix, which is 53 MPa for PET [34]. The diameter of the glass fiber, d is 10.5 μm. σ_{uf} is 3450 MPa for E type glass fiber. When these data are substituted into equation 4.1 critical fiber length was calculated as 342 μm. Since the values obtained from fiber length measurements are mostly higher than the critical length, the fibers will not be pull out from the matrix easily. Thus, an improved adhesion and in turn improved mechanical properties are obtained for the composites.

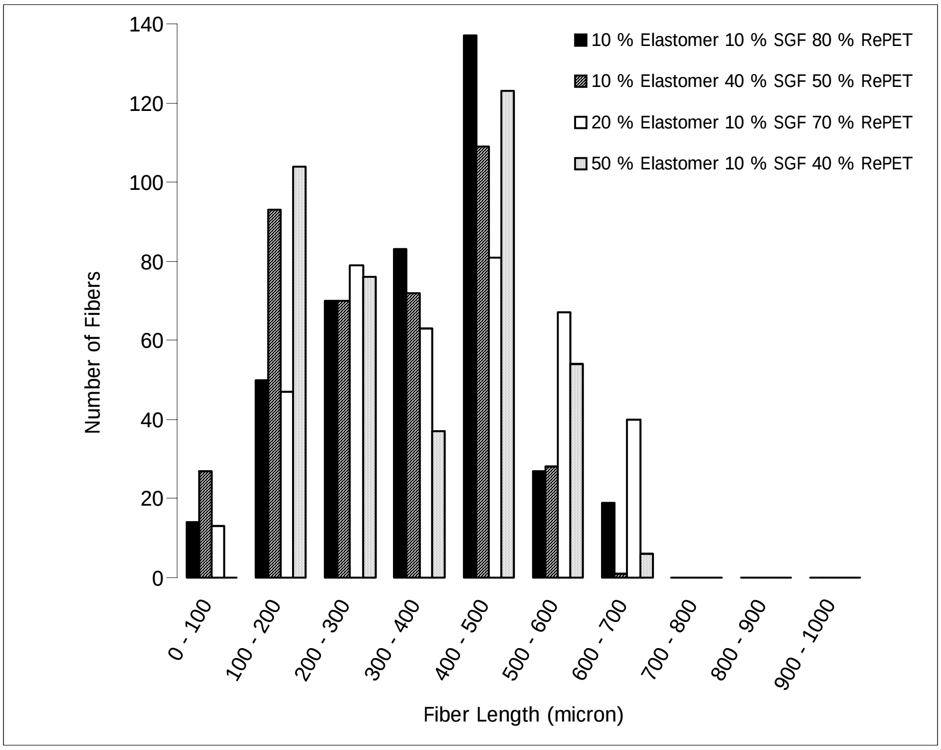


Figure 4.32 Fiber length distributions for selected ternary composites

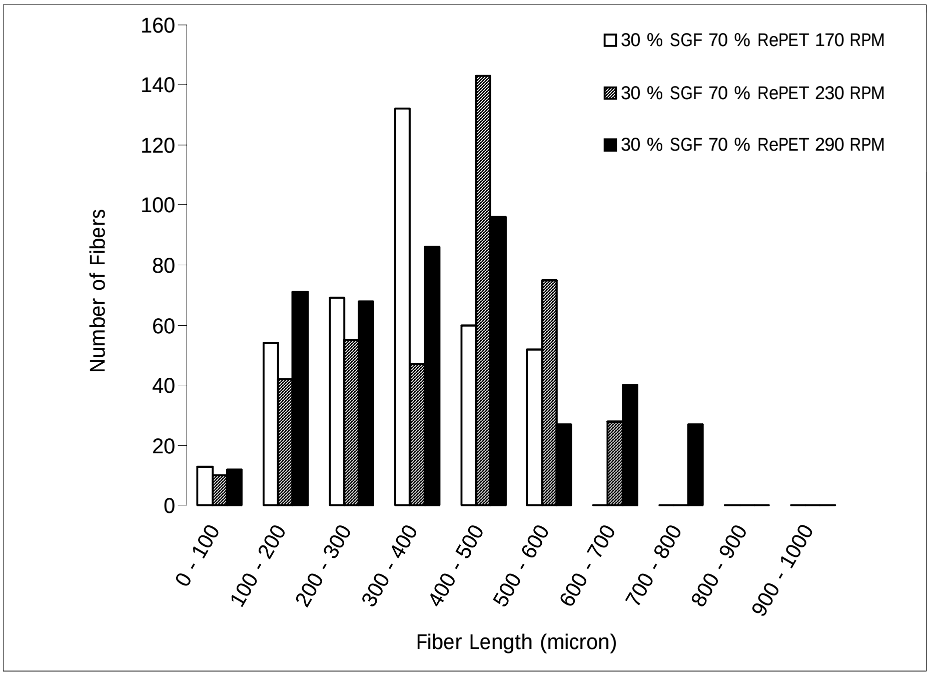


Figure 4.33 Fiber length distributions for effect of screw speed on SGF-recycled PET composites

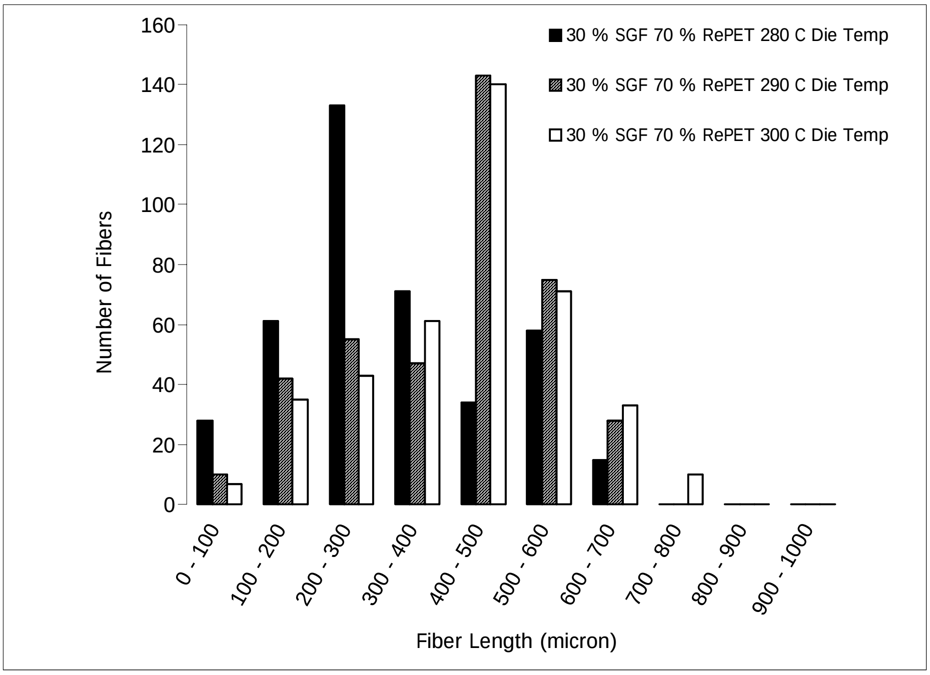


Figure 4.34 Fiber length distributions for effect of temperature profile on SGF-recycled PET composites

4.3.1 Dependence of mechanical properties of glass fiber-recycled PET composites on number average fiber length

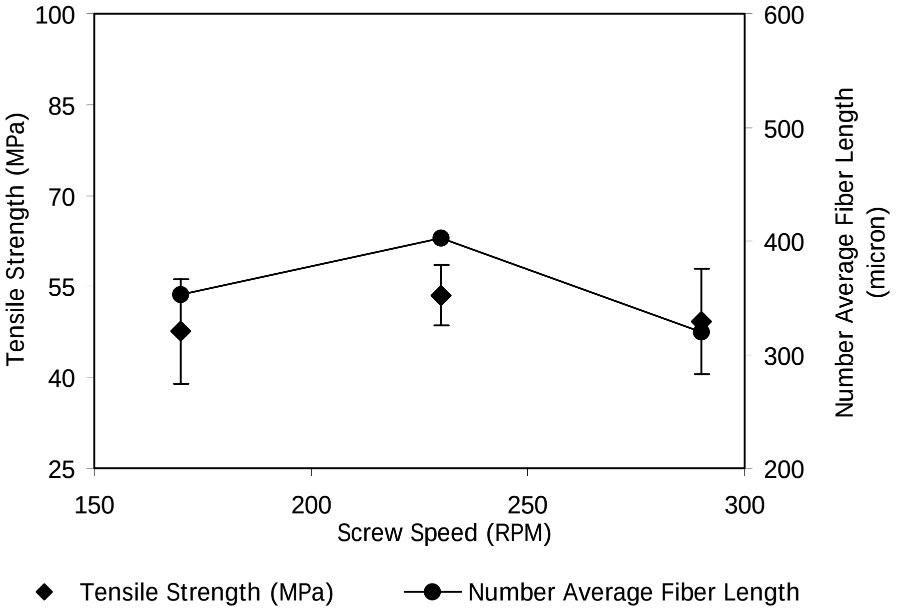


Figure 4.35 Dependence of tensile strength on number average fiber length and screw speed

The change in tensile strength with respect to temperature profile and average fiber length is illustrated in Figure 4.35. Tensile strength of a short fiber reinforced matrix improves as the fiber length increases. This is true for an increase in screw speed from 170 to 230 rpm. When the screw speed is increased further, both average fiber length and tensile strength decrease.

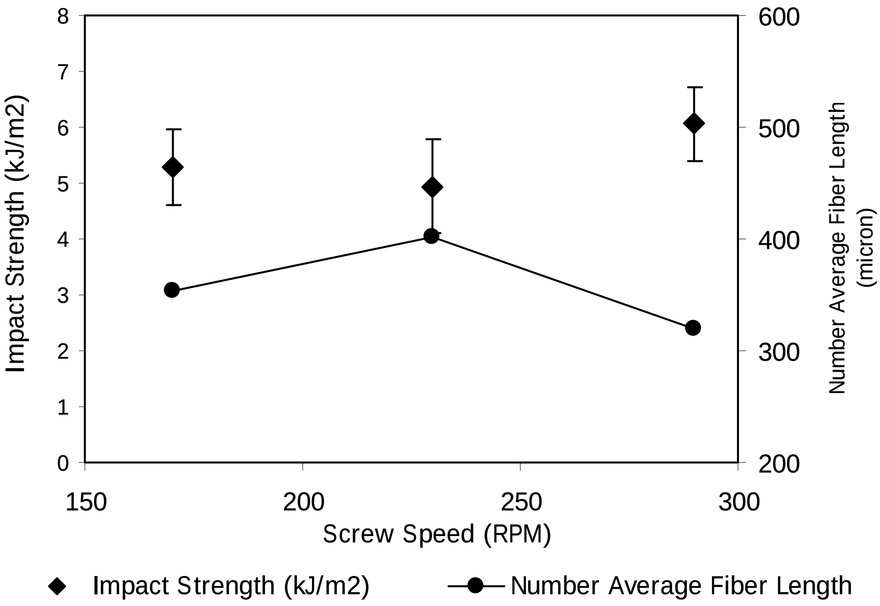


Figure 4.36 Dependence of impact strength on number average fiber length and screw speed

Unnotched charpy impact strength values with respect to screw speed and number average fiber length are shown in Figure 4.36. Number average fiber length shows a maximum at screw speed of 230 rpm. Impact strength values first decreases slightly from 170 rpm to 230 rpm, and then increases with further increase in screw speed.

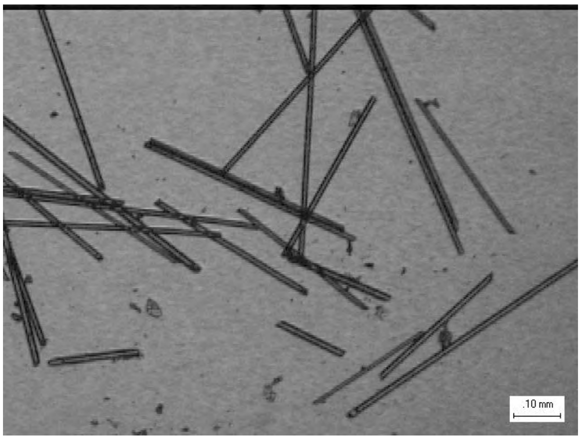


Figure 4.37 A sample photograph of dispersed fibers under microscope

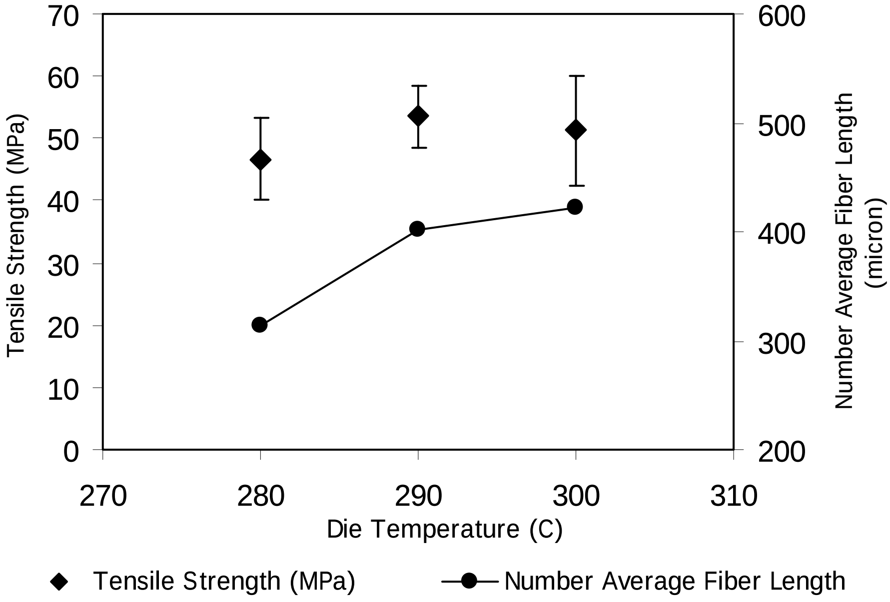


Figure 4.38 Dependence of tensile strength on number average fiber length and temperature profile

The change in tensile strength with respect to temperature profile and number average fiber length is illustrated in Figure 4.38. Increase in temperature profile decreases the viscosity of the system and as a result of low shear, the average fiber length increases. This will also contribute to the increase in tensile strength of the composites.

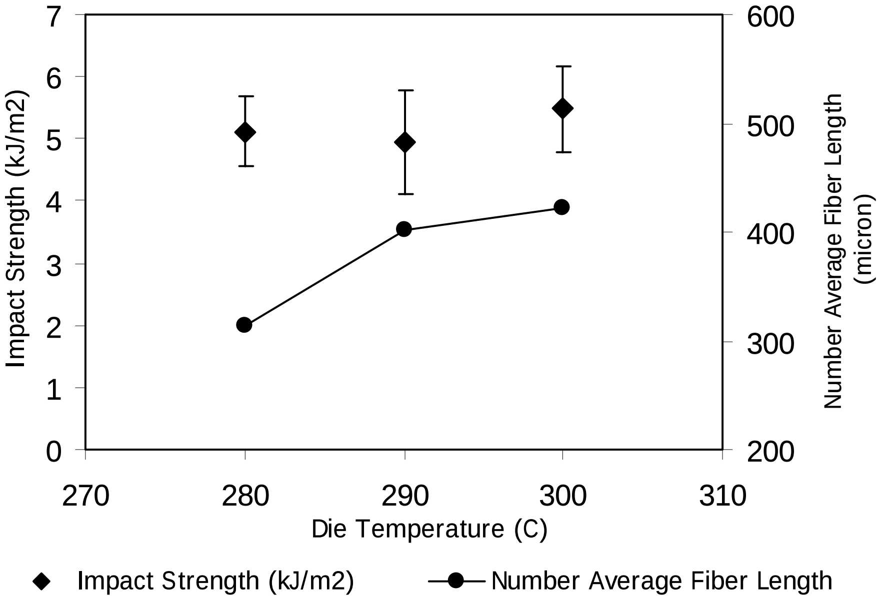


Figure 4.39 Dependence of impact strength on number average fiber length and temperature profile

A slight increase in the impact strength values of the composites with respect to processing temperature is shown in Figure 4.39. The reason of this increase can be due to the longer fibers which form high impact composites.

The effect of fiber length on mechanical properties of ternary composites is a complex phenomenon to explain because of the reactions involving in the system. It is claimed that, broad distributions of fibers might be effective in improving the mechanical properties of ternary system, but this may not be an evidence to find a reason on the changes in final properties.

4.4 Thermal Analysis

Tables 4.9 and 4.11 show the thermal properties of binary systems and ternary composites. In Table 4.9 explanation of the samples that were examined in terms of thermal analysis are given and, the effect of processing parameters such as temperature profile and screw speed on thermal properties are taken into account in Table 4.10.

The effects of glass fiber and elastomer contents in ternary composites are shown in Table 4.12, in which the materials studied, are given in Table 4.11.

In the tables, T_m, T_c, ΔH_c, ΔH_m and X_c represent melting temperature, crystallization temperature, heat of crystallization, heat of melting and percent crystallinity, respectively. Percent crystallinity values were calculated using the equation given below [48]

$$X_c = \frac{(\Delta H_m - \Delta H_c)}{\Delta H_m^0} x \frac{1}{w_{PET}} x 100 \qquad (4.2)$$

w_{PET} represents the weight fraction of PET in the blend/composite

Table 4.9 Samples studied to determine the influence of temperature and screw speed on thermal properties

Sample	Definition
N_1	30 % SGF – 70 % Re-PET (Die Temperature 280 °C)
N_2	30 % SGF – 70 % Re-PET (Die Temperature 290 °C)
N_3	30 % SGF – 70 % Re-PET (Die Temperature 300 °C)
N_4	30 % SGF – 70 % Re-PET (170 rpm)
N_5	30 % SGF – 70 % Re-PET (230 rpm)
N_6	30 % SGF – 70 % Re-PET (290 rpm)
N_7	30 % elastomer – 70 % Re-PET (Die Temperature 280 °C)
N_8	30 % elastomer – 70 % Re-PET (Die Temperature 290 °C)
N_9	30 % elastomer – 70 % Re-PET (Die Temperature 300 °C)
N_{10}	30 % elastomer – 70 % Re-PET (170 rpm)
N_{11}	30 % elastomer – 70 % Re-PET (230 rpm)
N_{12}	30 % elastomer – 70 % Re-PET (290 rpm)

Table 4.10 DSC results for the effect of screw speed and temperature profile on binary systems

	T_m (°C)	T_c (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_C (%)
N_1	254.61	134.46	60.30	94.62	35.5
N_2	254.72	135.12	50.84	75.14	25.1
N_3	251.52	136.23	53.14	34.02	19.8
N_4	253.79	135.68	52.03	78.14	27.0
N_5	254.72	135.12	50.84	75.14	25.1
N_6	254.12	134.47	46.63	72.45	26.7
N_7	251.18	137.87	48.38	47.78	0.6
N_8	251.27	136.14	44.14	45.21	1.1
N_9	252.32	142.06	33.18	33.85	0.5
N_{10}	249.12	137.62	28.71	28.56	0.1
N_{11}	251.27	136.14	44.14	45.21	1.1
N_{12}	250.01	134.80	33.13	38.43	5.5

ΔH_m^0 of a 100 % crystalline PET was taken as 138 J/g [39].

Table 4.11 Samples studied in content of ternary composites

Sample	Elastomer (%)	SGF (%)	re-PET (%)
S_1	10	10	80
S_2	10	20	70
S_3	10	30	60
S_4	10	40	50
S_5	20	10	70
S_6	20	20	60
S_7	20	30	50
S_8	20	40	40
S_9	30	10	60
S_{10}	30	20	50
S_{11}	30	30	40
S_{12}	40	10	50
S_{13}	40	20	40
S_{14}	50	10	40

Table 4.12 Results of DSC Analyses for ternary composites

	T_m (°C)	T_c (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_C (%)
S_1	252.91	---	---	29.82	27.0
S_2	252.17	---	---	22.69	23.5
S_3	254.55	---	---	21.90	26.4
S_4	252.98	---	---	17.97	26.0
S_5	253.62	124.30	44.18	73.15	29.9
S_6	252.62	125.62	28.35	56.04	33.4
S_7	252.47	123.18	28.73	58.64	43.3
S_8	256.09	123.66	28.81	57.16	51.3
S_9	252.07	127.42	36.76	60.17	28.2
S_{10}	253.15	126.63	20.82	51.98	45.1
S_{11}	252.34	126.05	44.58	61.98	31.5
S_{12}	255.91	130.78	22.83	34.37	16.7
S_{13}	251.51	129.19	20.04	35.78	28.5
S_{14}	255.11	136.96	32.75	34.35	2.9

Recycled poly(ethylene terephtahlate) used in this study, has a glass transition temperature of 75,5 °C, melting temperature of 254.51 °C and a degree of crystallinity of 16.8 %. The high T_g and T_m values of PET are as a result of the rigidity or the aromatic portion of the polymer. In addition, another stiffening group known as carboxyl group is present in the structure of PET. From DSC results, it can be concluded that, the melting points of composites or blends in both ternary and binary systems are not affected significantly with the change in parameters studied.

Glass transition temperatures of the composites or blends in both ternary and binary systems could not be designated properly, that is why they are not presented in the results of thermal analyses of the materials. Also some values of T_c and ΔH_c could not be observed due to the absence of the related peaks in DSC thermograms.

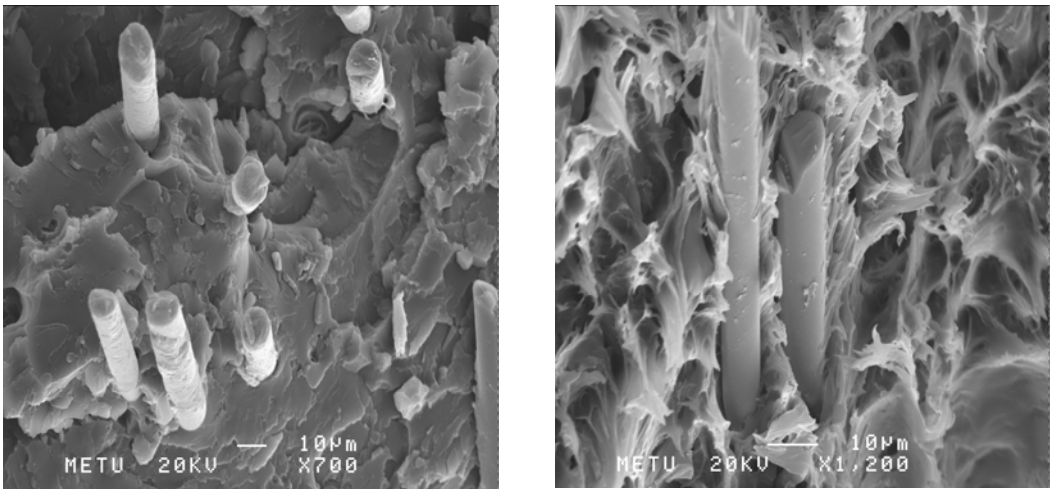
The degree of crystallinity of the composites decreases with the increase of elastomer content due to amorphous structure of elastomer.

4.5 Morphological Analysis

4.5.1 SEM analyses of ternary systems

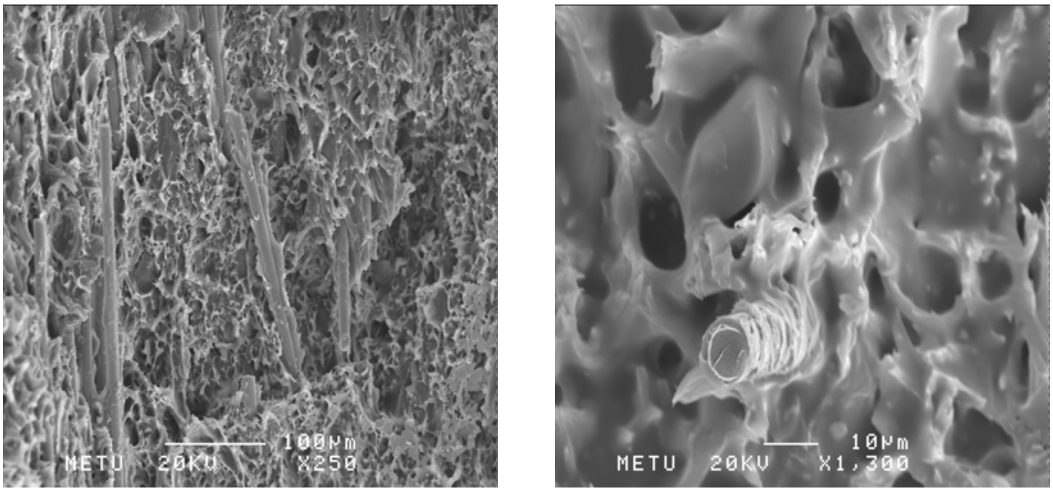
In the SEM analysis, photographs of ternary system are mainly given in Figures from 4.40 to 4.53 to observe the effects of glass fiber and the elastomer on the morphologies of ternary composites. Two different magnifications for each composition are provided for better observation.

The SEM photographs of the ternary composites designate that, the adhesion between fibers and the matrix is good, which is an indication of the improved mechanical properties. As seen in the figures such as Figure 4.40 and 4.51, adhesion between fiber and matrix increases with increasing elastomer content.



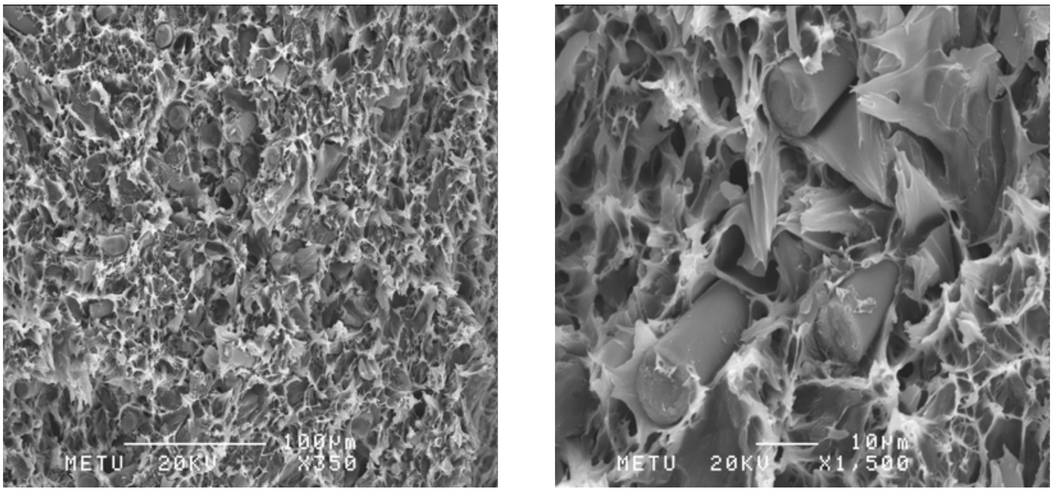
(a) **(b)**

Figure 4.40 SEM micrographs of composite containing 10 % elastomer – 10 % SGF – 80 % recycled PET



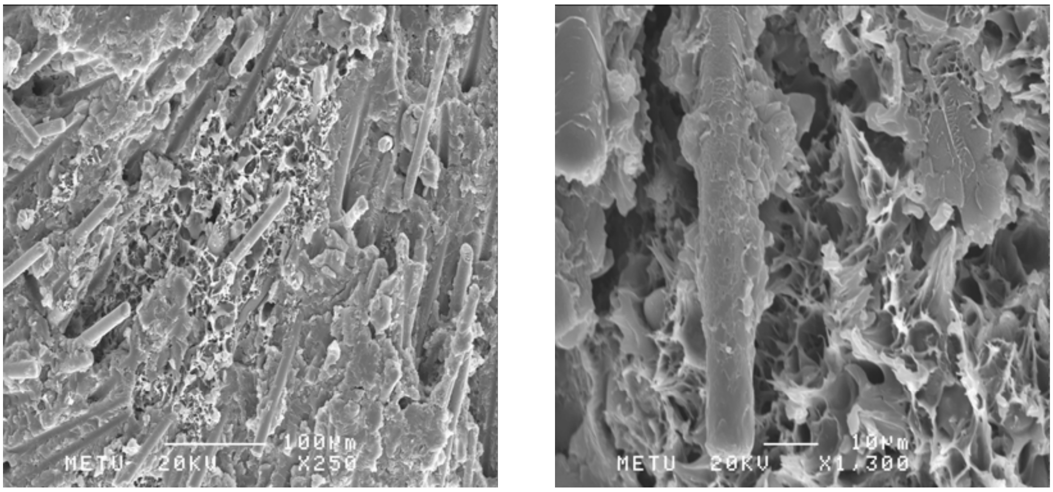
(a) **(b)**

Figure 4.41 SEM micrographs of composite containing 10 % elastomer – 20 % SGF – 70 % recycled PET



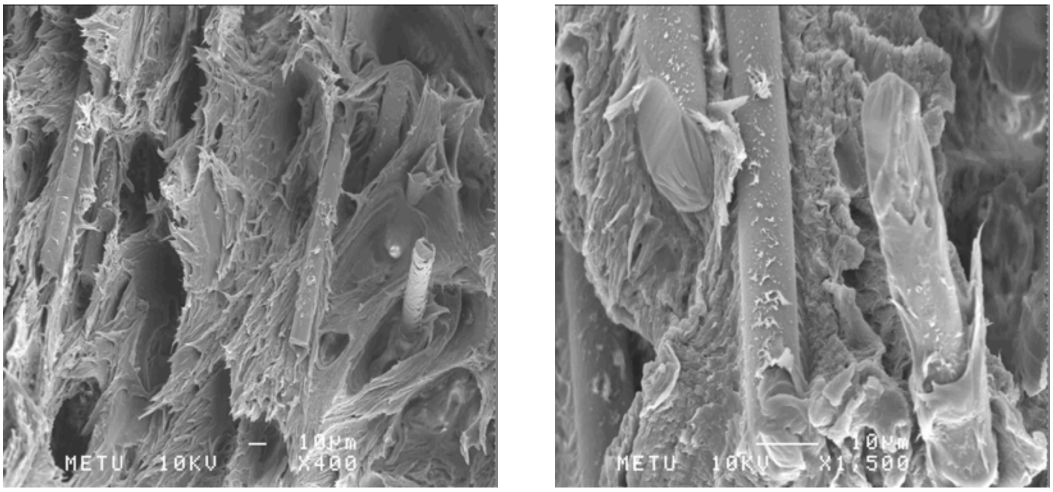
(a) **(b)**

Figure 4.42 SEM micrographs of composite containing 10 % elastomer – 30 % SGF – 60 % recycled PET



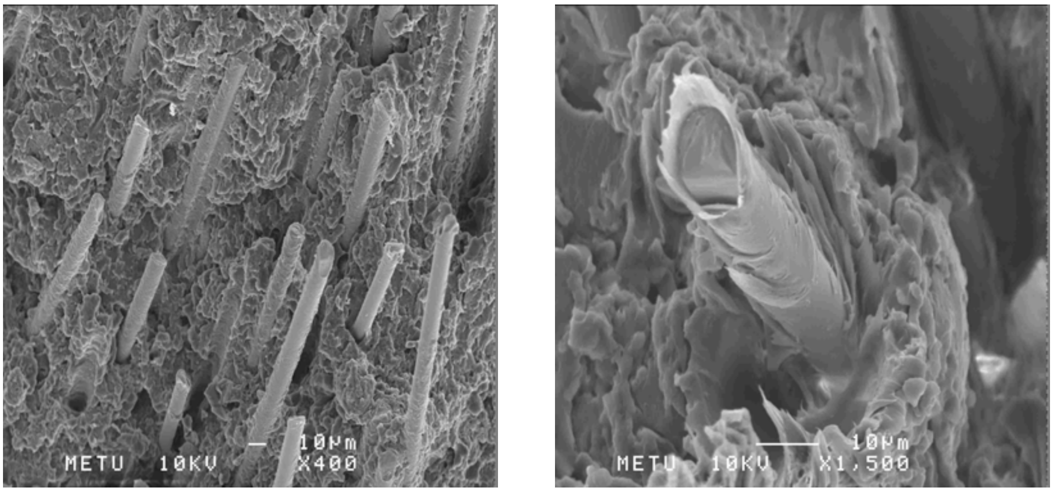
(a) **(b)**

Figure 4.43 SEM micrographs of composite containing 10 % elastomer – 40 % SGF – 50 % recycled PET



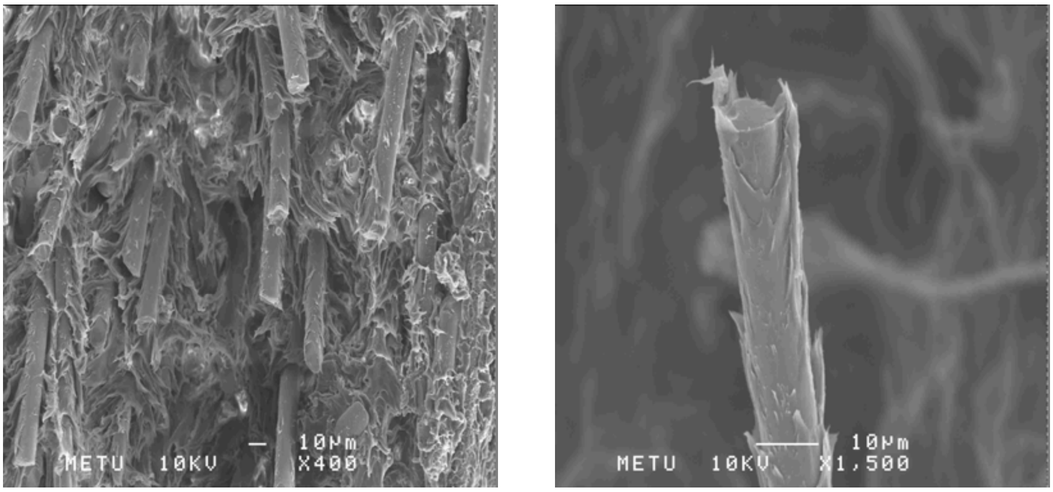
(a) **(b)**

Figure 4.44 SEM micrographs of composite containing 20 % elastomer – 10 % SGF – 70 % recycled PET



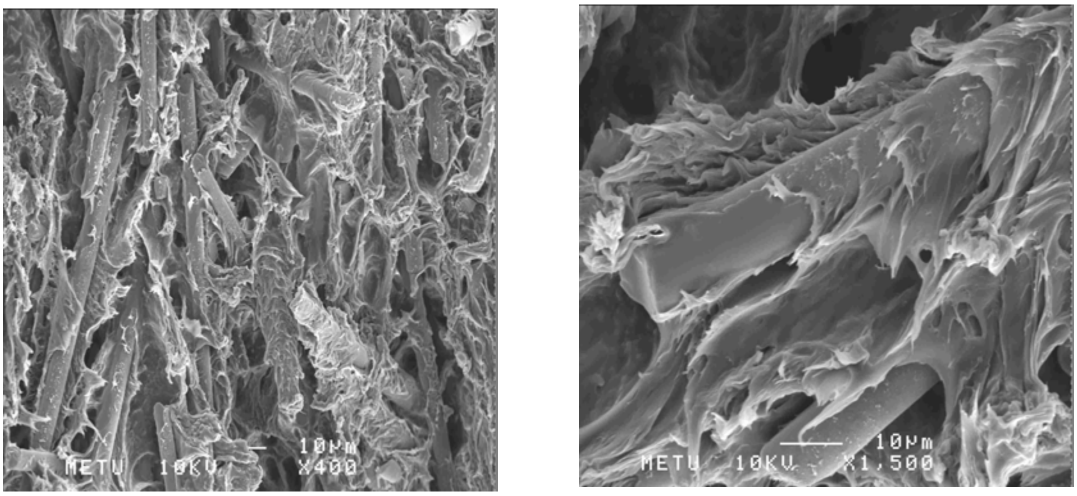
(a) **(b)**

Figure 4.45 SEM micrographs of composite containing 20 % elastomer – 20 % SGF – 60 % recycled PET



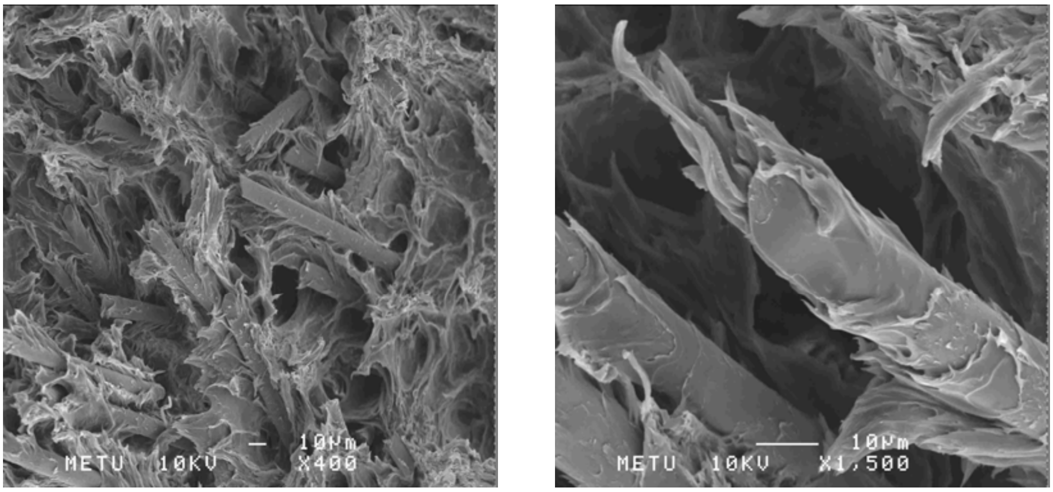
(a) (b)

Figure 4.46 SEM micrographs of composite containing 20 % elastomer – 30 % SGF – 50 % recycled PET



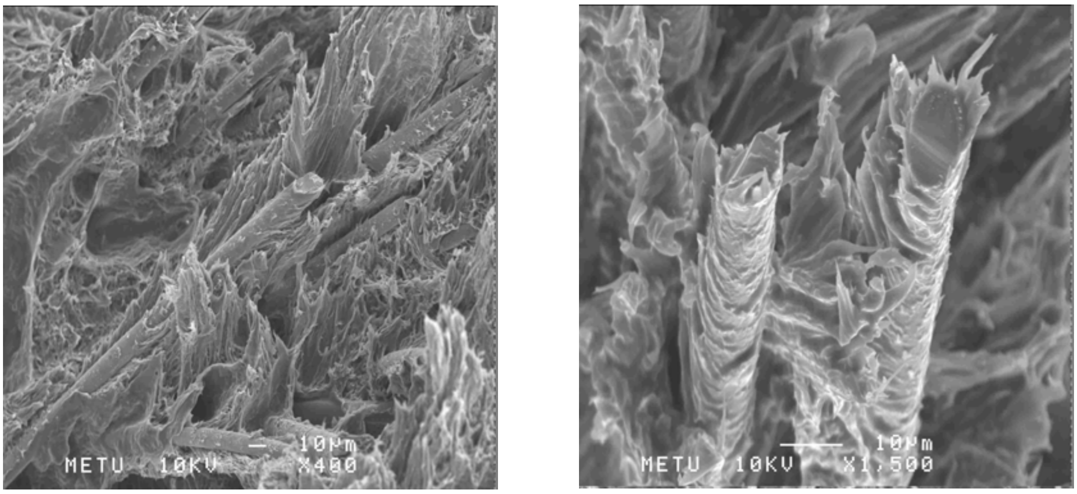
(a) (b)

Figure 4.47 SEM micrographs of composite containing 20 % elastomer – 40 % SGF – 40 % recycled PET



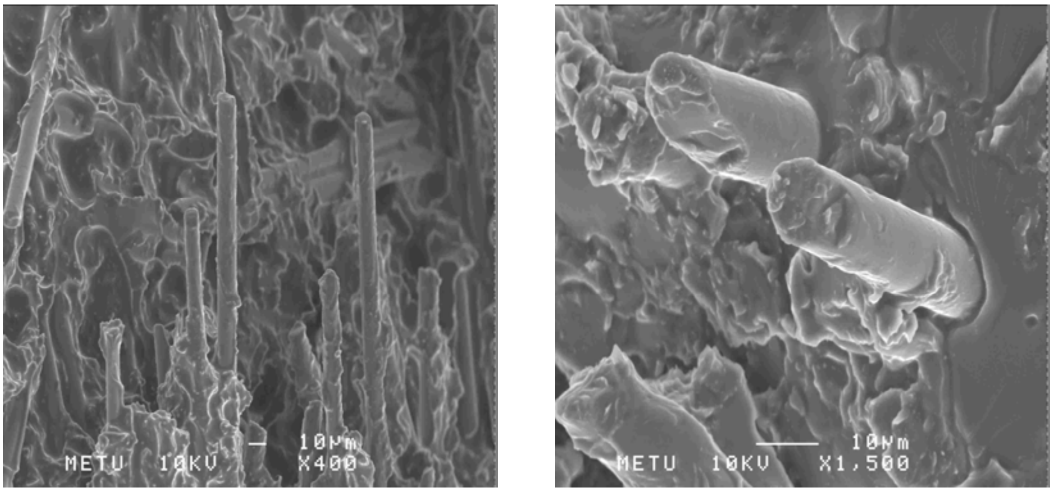
(a) **(b)**

Figure 4.48 SEM micrographs of composite containing 30 % elastomer – 10 % SGF – 60 % recycled PET



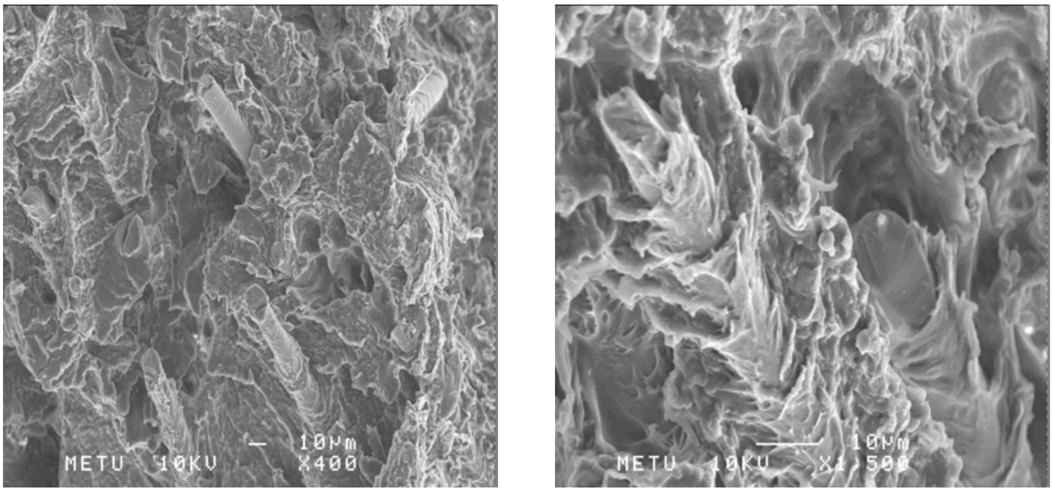
(a) **(b)**

Figure 4.49 SEM micrographs of composite containing 30 % elastomer – 20 % SGF – 50 % recycled PET



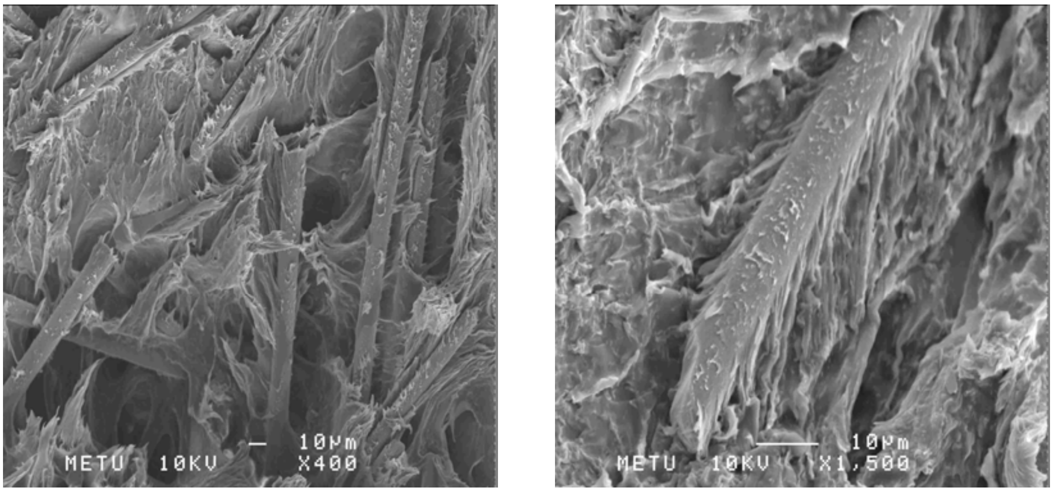
(a) **(b)**

Figure 4.50 SEM micrographs of composite containing 30 % elastomer – 30 % SGF – 40 % recycled PET



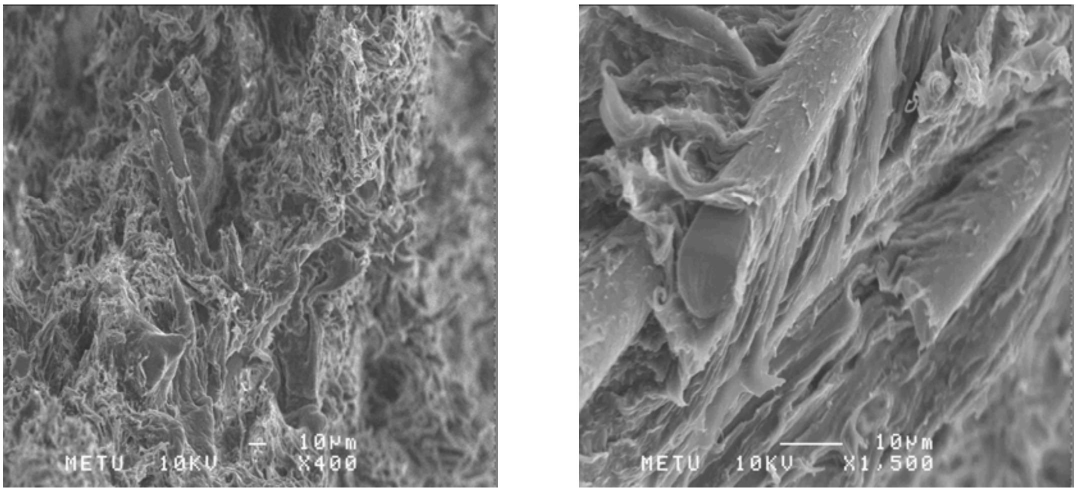
(a) **(b)**

Figure 4.51 SEM micrographs of composite containing 40 % elastomer – 10 % SGF – 50 % recycled PET



(a) **(b)**

Figure 4.52 SEM micrographs of composite containing 40 % elastomer – 20 % SGF – 40 % recycled PET

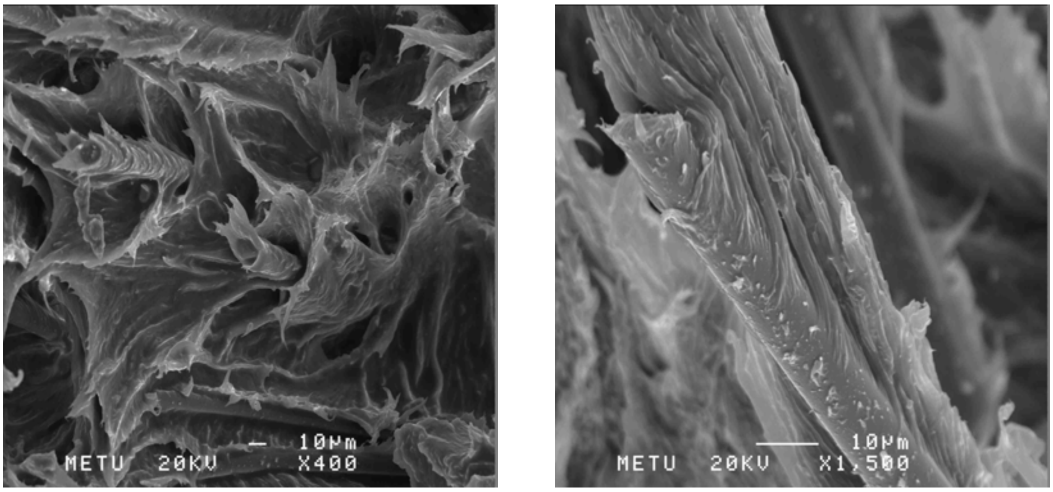


(a) **(b)**

Figure 4.53 SEM micrographs of composite containing 50 % elastomer – 10 % SGF – 40 % recycled PET

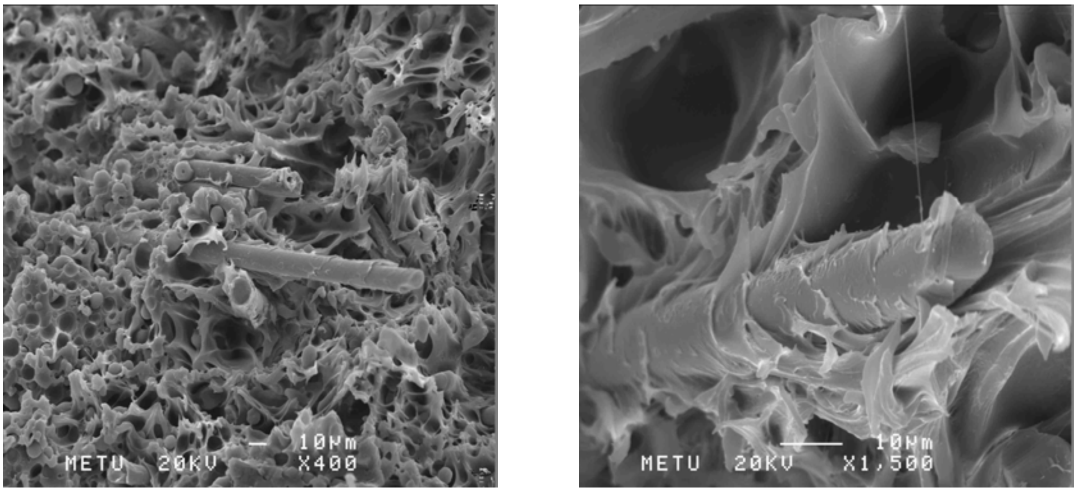
4.5.2 SEM analyses for effect of elastomer type on the morphologies of ternary composites

SEM micrographs of different elastomer types show good adhesion between fibers and matrix except composites containing Elvaloy 1224 AC (Figure 4.55) and Lotryl 28 MA 07 (Figure 4.56). In the micrographs of the composite with Elvaloy 1224 AC, there are minor immiscible phases which can easily be seen due to lack of functional group. In SEM micrographs of the composites containing Lotryl 28 MA 07, there are again immiscible phases as a result of the lack of functional groups such as GMA, which exists in Lotader AX8900 showing fine structure in Figure 4.45. Lotryl 28 MA 07 is not compatible with PET. This phenomenon was also supported by the low mechanical properties of the composites including Lotryl 28 MA 07.



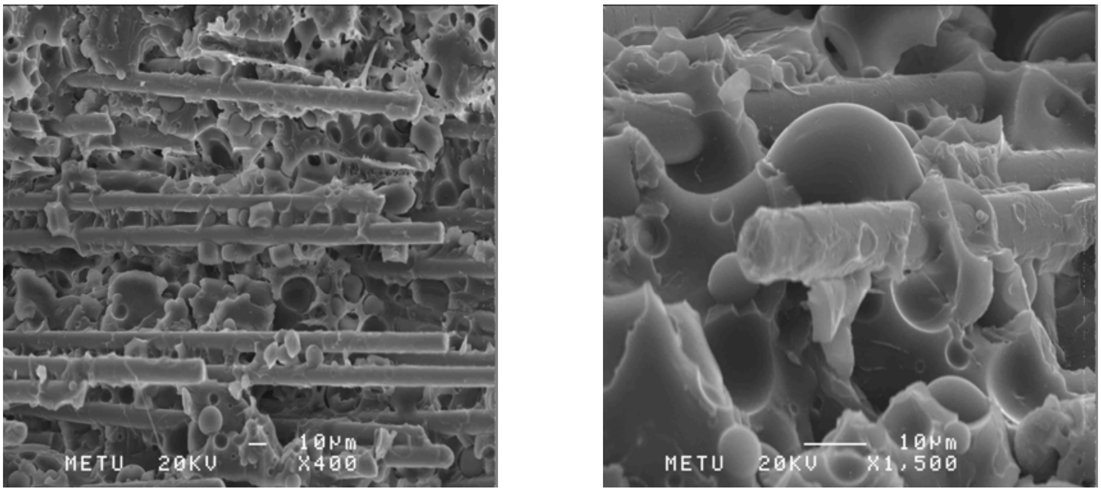
(a) (b)

Figure 4.54. SEM micrographs of composite containing 20 % elastomer – 20 % SGF – 60 % recycled PET including Elvaloy PTW Elastomer



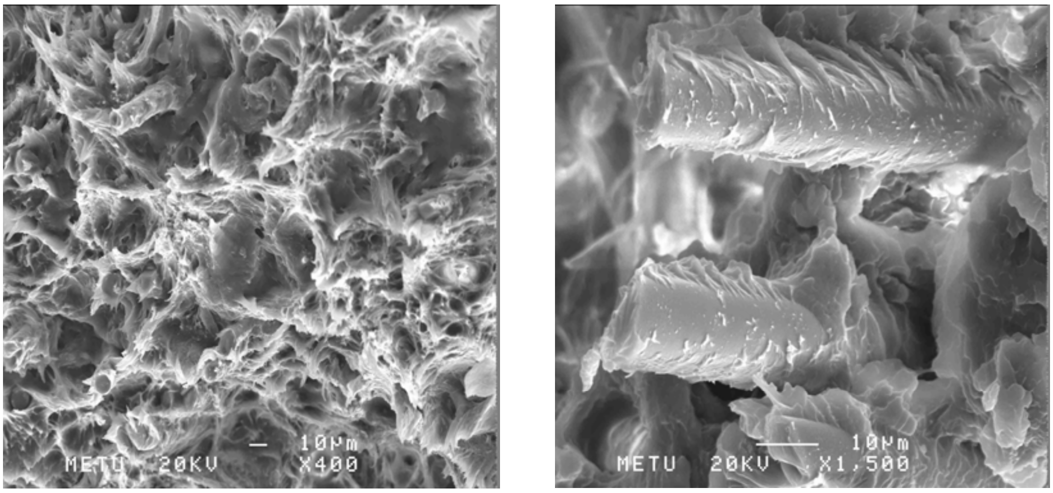
(a) **(b)**

Figure 4.55 SEM micrographs of composite containing 20 % elastomer – 20 % SGF – 60 % recycled PET including Elvaloy 1224 AC Elastomer



(a) **(b)**

Figure 4.56 SEM micrographs of composite containing 20 % elastomer – 20 % SGF – 60 % recycled PET including Lotryl 28 MA 07 Elastomer

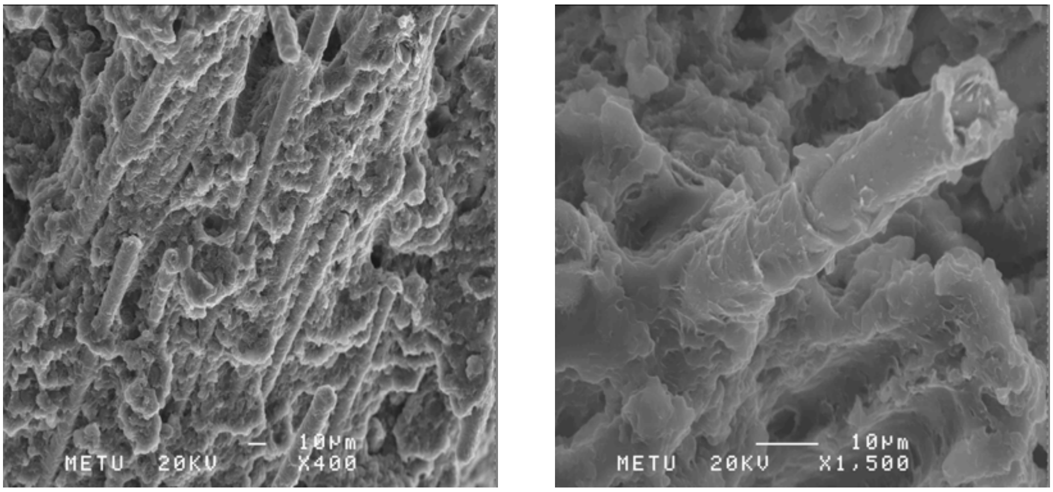


(a) **(b)**

Figure 4.57 SEM micrographs of composite containing 20 % elastomer – 20 % SGF – 60 % recycled PET including Lotader AX8840 Elastomer

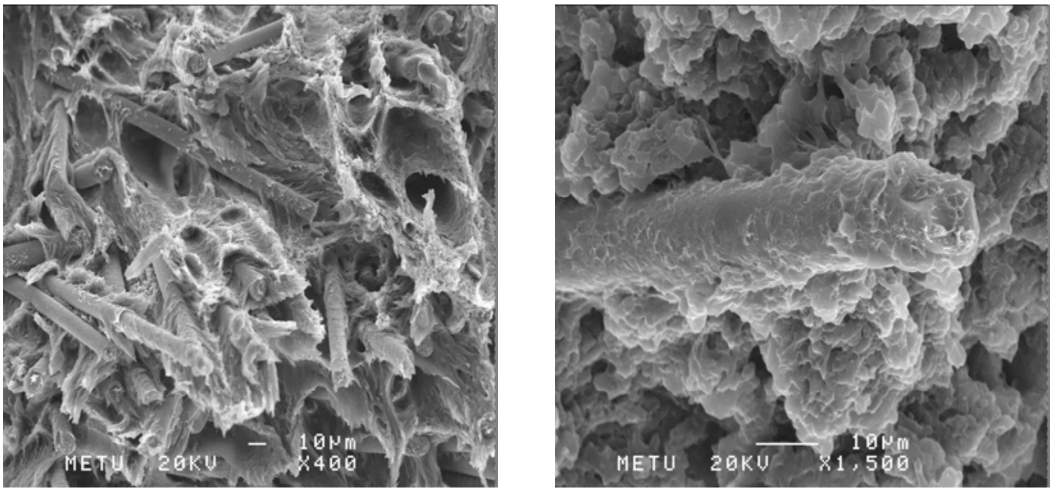
4.5.3 SEM analyses for effect of mixing protocol on the morphologies of ternary composites

There are not any significant differences in SEM micrographs of different types of mixing protocols as shown in Figures 4.58, 4.59 and 4.60, again good adhesion was observed in all mixing protocols.



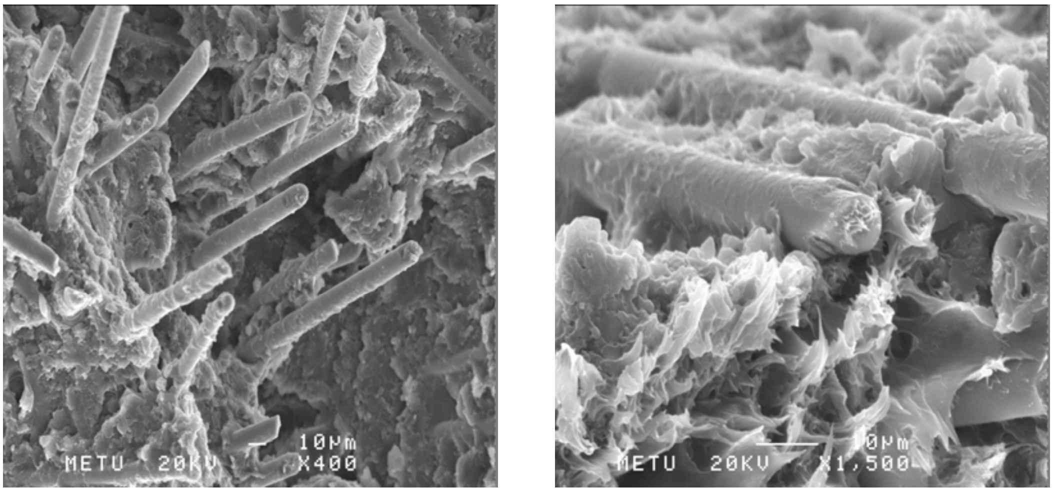
(a) **(b)**

Figure 4.58 SEM micrographs of effect of mixing protocol 1 on composite containing 20 % elastomer – 20 % SGF – 60 % recycled PET



(a) **(b)**

Figure 4.59 SEM micrographs of effect of mixing protocol 2 on composite containing 20 % elastomer – 20 % SGF – 60 % recycled PET



(a) **(b)**

Figure 4.60 SEM micrographs of effect of mixing protocol 3 on composite containing 20 % elastomer – 20 % SGF – 60 % recycled PET

CHAPTER V

CONCLUSIONS

Ternary composites of elastomer-glass fiber-recycled PET were obtained in a wide range of different compositions. This wide range enables one to determine the mechanical properties of the composites for some significant application fields, such as impact strength significant applications and/or tensile modulus significant applications. The produced composites were characterized in terms of mechanical, thermal and morphological properties. Their melt flow behavior and fiber length distributions were also investigated.

For comparison, binary composites including glass fiber and recycled PET; binary blends with elastomer and recycled PET were produced at different compositions. Extrusion process parameters, such as screw speed, temperature profile were examined, for the binary systems. The information obtained from here was used for processing of ternary composites.

Lastly to improve ternary composites further, different types of elastomers were tried at one selected composition of the ternary system, and also at that selected composition, different mixing sequences in extrusion were examined. Characterizations of these composites also were done in terms of mechanical properties and morphologies.

Ternary composites showed different mechanical properties than binary systems. In general, glass fiber in the composite prevented reduction of tensile strength and moduli up to 20 % percent elastomer containing ternary composites when compared with the glass fiber-recycled binary composites. Beyond 20 % elastomer composition, tensile strength and moduli decreased with respect to those of binary composites due to the flexibility dominant effect of elastomer. When compared with elastomer-recycled PET binary blends, tensile strength and modulus data of ternary composites were higher up to elastomer concentration of 20-30 %. Impact strength of ternary composites increased significantly after 30 % elastomer content. When the overall mechanical properties are considered, ternary composite, 20 % elastomer-20 % glass fiber-60 % recycled PET composition was selected for further experiments. When this ternary composite was compared with 20 % glass fiber-80 % recycled PET binary composite and 20 % elastomer-recycled PET binary blend, tensile strength was increased 26.7 % with respect to elastomer including binary blend and decreased 27.2 % with respect to glass fiber including binary composite, but impact strength of the ternary composite was increased 65.9 % in comparison to binary blend and increased 470.3 % when compared with binary composite. A suitable composition could be selected for considering the application field of the materials according to which mechanical properties are more important.

DSC analyses showed that melting points of the ternary composites did not change significantly at different compositions of glass fiber and elastomer, and degree of crystallinities were decreased with increasing elastomer.

It was seen from SEM analyses that there was a good adhesion between the fibers and the matrix material, and the adhesion increased with the increase of elastomer content. The fine morphologies obtained for the composites including Lotader AX8900 showed that this epoxy functional elastomer was compatible with recycled PET and there was a possibility of some reactions occurring between recycled PET and elastomer. When Lotryl 28 MA 07, which does not have epoxy functionality, was used in ternary composites, immiscible phases were observed. This indicates lack of adhesion which would be the reason for poor mechanical properties of these composites.

MFI results showed that the viscosity of the ternary composites increased with increasing both glass fiber and elastomer concentrations. This indicates the molecular weight increase due to the potential reactions between elastomer and PET. Also, there would be some reactions between amine groups of glass fiber surface and epoxy groups of elastomer which would increase the adhesion.

In the selected work range of extrusion process parameters such as, screw speed and temperature profile, mechanical properties of binary composites and binary blends were not affected significantly. As expected, on one side, binary composites gave better tensile strength and moduli values, on the other side binary blends gave better impact strength values.

When fiber length distribution was analyzed for the effect of extrusion parameters on glass fiber-recycled PET composites, the number average fiber length values were determined as higher than critical fiber length that also indicates the existence of good adhesion between fibers and the matrix.

When effect of elastomer type on ternary composites was examined, it was seen that Lotryl 28 MA 07 elastomer gave lowest tensile properties than other elastomers due to lack of its epoxy functional group. Elvaloy PTW type elastomer gave the best impact strength result. Lotader AX8900 containing composite had the highest tensile modulus value among the others.

Lastly, effect of mixing protocol in extrusion was examined. Other than the original protocol, three different sequence of addition was tried on selected ternary composite. There were minor changes, but when overall properties were considered original protocol had better results as in this protocol materials were extruded once and in other protocols materials were extruded twice.

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APPENDIX A

A.1 Tensile Strength Results for All Sets

Table A.1.1 Tensile Strength Data for Set II

Composite	Tensile Strength (MPa)	Stand. Dev.
10 % SGF – 90 % re-PET	33	7.3
20 % SGF – 80 % re-PET	42	2.1
30 % SGF – 70 % re-PET	53	4.9
40 % SGF – 60 % re-PET	46	2.7
50 % SGF – 50 % re-PET	37	4.2

Table A.1.2 Tensile Strength Data for Set III

Blend	Tensile Strength (MPa)	Stand. Dev.
10 % elastomer – 90 % re-PET	33	1.2
20 % elastomer – 80 % re-PET	24	0.6
30 % elastomer – 70 % re-PET	19	0.5
40 % elastomer – 60 % re-PET	15	1.2
50 % elastomer – 50 % re-PET	12	0.8

Table A.1.3 Tensile Strength Data for Set IV (Effect of Screw Speed)

Composite	Tensile Strength (MPa)	Stand. Dev.
30 % SGF – 70 % re-PET 170 rpm	47	8.7
30 % SGF – 70 % re-PET 230 rpm	53	4.9
30 % SGF – 70 % re-PET 290 rpm	49	9.4

Table A.1.4 Tensile Strength Data for Set IV (Effect of Temperature Profile)

Composite	Tensile Strength (MPa)	Stand. Dev.
30 % SGF – 70 % re-PET 280 °C Die Temperature	47	6.7
30 % SGF – 70 % re-PET 290 °C Die Temperature	53	4.9
30 % SGF – 70 % re-PET 300 °C Die Temperature	51	8.7

Table A.1.5 Tensile Strength Data for Set V (Effect of Screw Speed)

Blend	Tensile Strength (MPa)	Stand. Dev.
30 % elastomer – 70 % re-PET 170 rpm	18	2.5
30 % elastomer – 70 % re-PET 230 rpm	19	3.1
30 % elastomer – 70 % re-PET 290 rpm	20	2.0

Table A.1.6 Tensile Strength Data for Set V (Effect of Temperature Profile)

Blend	Tensile Strength (MPa)	Stand. Dev.
30 % elastomer – 70 % re-PET 280 °C Die Temperature	19	0.4
30 % elastomer – 70 % re-PET 290 °C Die Temperature	19	3.1
30 % elastomer – 70 % re-PET 300 °C Die Temperature	20	1.9

Table A.1.7 Tensile Strength Data for Set VI

Composite	Tensile Strength (MPa)	Stand. Dev.
10 % elastomer – 10 % SGF - 80 % re-PET	38	1.3
10 % elastomer – 20 % SGF - 70 % re-PET	39	1.6
10 % elastomer – 30 % SGF - 60 % re-PET	39	2.0
10 % elastomer – 40 % SGF - 50 % re-PET	34	1.9
20 % elastomer – 10 % SGF - 70 % re-PET	29	0.7
20 % elastomer – 20 % SGF - 60 % re-PET	30	1.0
20 % elastomer – 30 % SGF - 50 % re-PET	25	1.4
20 % elastomer – 40 % SGF - 40 % re-PET	21	0.1
30 % elastomer – 10 % SGF - 60 % re-PET	15	1.0
30 % elastomer – 20 % SGF - 50 % re-PET	15	0.6
30 % elastomer – 30 % SGF - 40 % re-PET	14	0.7
40 % elastomer – 10 % SGF - 50 % re-PET	17	0.6
40 % elastomer – 20 % SGF - 40 % re-PET	14	0.8
50 % elastomer – 10 % SGF - 40 % re-PET	10	0.3

Table A.1.8 Tensile Strength Data for Set VII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Tensile Strength (MPa)	Stand. Dev.
Elvaloy PTW	29	0.9
Elvaloy 1224 AC	35	2.2
Lotryl 28 MA 07	25	1.0
Lotader AX 8840	30	0.8
Lotader AX 8900	30	1.0

Table A.1.9 Tensile Strength Data for Set VIII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Tensile Strength (MPa)	Stand. Dev.
Mixing Protocol 1	27	0.2
Mixing Protocol 2	26	0.1
Mixing Protocol 3	30	0.5
Original Mixing Protocol	30	1.0

A.2 Tensile Modulus Results For All Sets

Table A.2.1 Tensile Modulus Data for Set II

Composite	Tensile Modulus (MPa)	Stand. Dev.
10 % SGF – 90 % re-PET	1295	91.1
20 % SGF – 80 % re-PET	1317	187.6
30 % SGF – 70 % re-PET	1969	182.6
40 % SGF – 60 % re-PET	2076	225.9
50 % SGF – 50 % re-PET	1902	345.5

Table A.2.2 Tensile Modulus Data for Set III

Blend	Tensile Modulus (MPa)	Stand. Dev.
10 % elastomer – 90 % re-PET	1278	16.8
20 % elastomer – 80 % re-PET	958	22.7
30 % elastomer – 70 % re-PET	559	92.2
40 % elastomer – 60 % re-PET	479	10.0
50 % elastomer – 50 % re-PET	401	64.0

Table A.2.3 Tensile Modulus Data for Set IV (Effect of Screw Speed)

Composite	Tensile Modulus (MPa)	Stand. Dev.
30 % SGF – 70 % re-PET 170 rpm	2127	236.0
30 % SGF – 70 % re-PET 230 rpm	1969	182.6
30 % SGF – 70 % re-PET 290 rpm	2007	164.6

Table A.2.4 Tensile Modulus Data for Set IV (Effect of Temperature Profile)

Composite	Tensile Modulus (MPa)	Stand. Dev.
30 % SGF – 70 % re-PET 280 °C Die Temperature	2140	190.6
30 % SGF – 70 % re-PET 290 °C Die Temperature	1969	182.6
30 % SGF – 70 % re-PET 300 °C Die Temperature	2050	190.6

Table A.2.5 Tensile Modulus Data for Set V (Effect of Screw Speed)

Blend	Tensile Modulus (MPa)	Stand. Dev.
30 % elastomer – 70 % re-PET 170 rpm	603	61.5
30 % elastomer – 70 % re-PET 230 rpm	559	70.1
30 % elastomer – 70 % re-PET 290 rpm	539	92.2

Table A.2.6 Tensile Modulus Data for Set V (Effect of Temperature Profile)

Blend	Tensile Modulus (MPa)	Stand. Dev.
30 % elastomer – 70 % re-PET 280 °C Die Temperature	567	87.2
30 % elastomer – 70 % re-PET 290 °C Die Temperature	559	70.1
30 % elastomer – 70 % re-PET 300 °C Die Temperature	548	56.3

Table A.2.7 Tensile Modulus data for Set VI

Composite	Tensile Modulus (MPa)	Stand. Dev.
10 % elastomer – 10 % SGF - 80 % re-PET	1721	27.6
10 % elastomer – 20 % SGF - 70 % re-PET	1684	20.3
10 % elastomer – 30 % SGF - 60 % re-PET	1741	10.0
10 % elastomer – 40 % SGF - 50 % re-PET	1666	69.5
20 % elastomer – 10 % SGF - 70 % re-PET	1514	108.4
20 % elastomer – 20 % SGF - 60 % re-PET	1369	10.0
20 % elastomer – 30 % SGF - 50 % re-PET	1109	76.9
20 % elastomer – 40 % SGF - 40 % re-PET	925	71.4
30 % elastomer – 10 % SGF - 60 % re-PET	699	86.4
30 % elastomer – 20 % SGF - 50 % re-PET	680	49.7
30 % elastomer – 30 % SGF - 40 % re-PET	706	34.0
40 % elastomer – 10 % SGF - 50 % re-PET	508	89.5
40 % elastomer – 20 % SGF - 40 % re-PET	456	26.0
50 % elastomer – 10 % SGF - 40 % re-PET	277	23.1

Table A.2.8 Tensile Modulus Data for Set VII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Tensile Modulus (MPa)	Stand. Dev.
Elvaloy PTW	1227	145.3
Elvaloy 1224 AC	1288	24.4
Lotryl 28 MA 07	1169	141.3
Lotader AX 8840	1251	146.1
Lotader AX 8900	1369	10.0

Table A.2.9 Tensile Modulus Data for Set VIII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Tensile Modulus (MPa)	Stand. Dev.
Mixing Protocol 1	1206	81.2
Mixing Protocol 2	1607	48.0
Mixing Protocol 3	1988	103.1
Original Mixing Protocol	1369	10.0

A.3 Elongation at break Results For All Sets

Table A.3.1 Elongation at break Data for Set II

Composite	Elongation at break (%)	Stand. Dev.
10 % SGF – 90 % re-PET	3	0.1
20 % SGF – 80 % re-PET	3	0.6
30 % SGF – 70 % re-PET	3	0.4
40 % SGF – 60 % re-PET	2	0.4
50 % SGF – 50 % re-PET	2	0.2

Table A.3.2 Elongation at break Data for Set III

Blend	Elongation at break (%)	Stand. Dev.
10 % elastomer – 90 % re-PET	48	5.5
20 % elastomer – 80 % re-PET	80	8.2
30 % elastomer – 70 % re-PET	74	16.6
40 % elastomer – 60 % re-PET	76	15.4
50 % elastomer – 50 % re-PET	59	1.6

Table A.3.3 Elongation at break Data for Set IV (Effect of Screw Speed)

Composite	Elongation at break (%)	Stand. Dev.
30 % SGF – 70 % re-PET 170 rpm	3	0.5
30 % SGF – 70 % re-PET 230 rpm	3	0.4
30 % SGF – 70 % re-PET 290 rpm	4	0.1

Table A.3.4 Elongation at break Data for Set IV (Effect of Temperature Profile)

Composite	Elongation at break (%)	Stand. Dev.
30 % SGF – 70 % re-PET 280 °C Die Temperature	3	0.3
30 % SGF – 70 % re-PET 290 °C Die Temperature	3	0.4
30 % SGF – 70 % re-PET 300 °C Die Temperature	3	0.4

Table A.3.5 Elongation at break Data for Set V (Effect of Screw Speed)

Blend	Elongation at break (%)	Stand. Dev.
30 % elastomer – 70 % re-PET 170 rpm	27	15.9
30 % elastomer – 70 % re-PET 230 rpm	74	16.6
30 % elastomer – 70 % re-PET 290 rpm	103	11.8

Table A.3.6 Elongation at break Data for Set V (Effect of Temperature Profile)

Blend	Elongation at break (%)	Stand. Dev.
30 % elastomer – 70 % re-PET 280 °C Die Temperature	72	13.2
30 % elastomer – 70 % re-PET 290 °C Die Temperature	74	16.6
30 % elastomer – 70 % re-PET 300 °C Die Temperature	81	9.6

Table A.3.7 Elongation at break Data for Set VI

Composite	Elongation at break (%)	Stand. Dev.
10 % elastomer – 10 % SGF - 80 % re-PET	5	0.3
10 % elastomer – 20 % SGF - 70 % re-PET	5	0.4
10 % elastomer – 30 % SGF - 60 % re-PET	5	0.1
10 % elastomer – 40 % SGF - 50 % re-PET	5	0.3
20 % elastomer – 10 % SGF - 70 % re-PET	15	0.9
20 % elastomer – 20 % SGF - 60 % re-PET	13	1.0
20 % elastomer – 30 % SGF - 50 % re-PET	6	0.4
20 % elastomer – 40 % SGF - 40 % re-PET	3	0.4
30 % elastomer – 10 % SGF - 60 % re-PET	5	0.2
30 % elastomer – 20 % SGF - 50 % re-PET	4	0.7
30 % elastomer – 30 % SGF - 40 % re-PET	4	1.1
40 % elastomer – 10 % SGF - 50 % re-PET	18	3.3
40 % elastomer – 20 % SGF - 40 % re-PET	10	2.5
50 % elastomer – 10 % SGF - 40 % re-PET	17	2.5

Table A.3.8 Elongation at break Data for Set VII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Elongation at break (%)	Stand. Dev.
Elvaloy PTW	8	0.6
Elvaloy 1224 AC	5	0.7
Lotryl 28 MA 07	3	0.3
Lotader AX 8840	7	0.5
Lotader AX 8900	13	1.0

Table A.3.9 Elongation at break Data for Set VIII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Elongation at break (%)	Stand. Dev.
Mixing Protocol 1	9	1.4
Mixing Protocol 2	7	0.8
Mixing Protocol 3	3	0.4
Original Mixing Protocol	13	1.0

A.4 Flexural Strength Results For All Sets

Table A.4.1 Flexural Strength Data for Set II

Composite	Flexural Strength (MPa)	Stand. Dev.
10 % SGF – 90 % re-PET	94	23.1
20 % SGF – 80 % re-PET	103	12.5
30 % SGF – 70 % re-PET	98	12.1
40 % SGF – 60 % re-PET	106	8.3
50 % SGF – 50 % re-PET	88	8.2

Table A.4.2 Flexural Strength Data for Set III

Blend	Flexural Strength (MPa)	Stand. Dev.
10 % elastomer – 90 % re-PET	52	1.0
20 % elastomer – 80 % re-PET	31	5.5
30 % elastomer – 70 % re-PET	27	1.6
40 % elastomer – 60 % re-PET	20	1.4
50 % elastomer – 50 % re-PET	16	3.6

Table A.4.3 Flexural Strength Data for Set IV (Effect of Screw Speed)

Composite	Flexural Strength (MPa)	Stand. Dev.
30 % SGF – 70 % re-PET 170 rpm	113	5.3
30 % SGF – 70 % re-PET 230 rpm	98	12.1
30 % SGF – 70 % re-PET 290 rpm	101	15.6

Table A.4.4 Flexural Strength Data for Set IV (Effect of Temperature Profile)

Composite	Flexural Strength (MPa)	Stand. Dev.
30 % SGF – 70 % re-PET 280 °C Die Temperature	111	9.8
30 % SGF – 70 % re-PET 290 °C Die Temperature	98	12.1
30 % SGF – 70 % re-PET 300 °C Die Temperature	105	12.8

Table A.4.5 Flexural Strength Data for Set V (Effect of Screw Speed)

Blend	Flexural Strength (MPa)	Stand. Dev.
30 % elastomer – 70 % re-PET 170 rpm	29	3.8
30 % elastomer – 70 % re-PET 230 rpm	27	1.6
30 % elastomer – 70 % re-PET 290 rpm	41	9.4

Table A.4.6 Flexural Strength Data for Set V (Effect of Temperature Profile)

Blend	Flexural Strength (MPa)	Stand. Dev.
30 % elastomer – 70 % re-PET 280 °C Die Temperature	28	9.9
30 % elastomer – 70 % re-PET 290 °C Die Temperature	27	1.6
30 % elastomer – 70 % re-PET 300 °C Die Temperature	32	5.6

Table A.4.7 Flexural Strength Data for Set VI

Composite	Flexural Strength (MPa)	Stand. Dev.
10 % elastomer – 10 % SGF - 80 % re-PET	37	3.3
10 % elastomer – 20 % SGF - 70 % re-PET	38	4.4
10 % elastomer – 30 % SGF - 60 % re-PET	39	5.1
10 % elastomer – 40 % SGF - 50 % re-PET	33	2.3
20 % elastomer – 10 % SGF - 70 % re-PET	32	0.9
20 % elastomer – 20 % SGF - 60 % re-PET	38	1.1
20 % elastomer – 30 % SGF - 50 % re-PET	46	1.7
20 % elastomer – 40 % SGF - 40 % re-PET	44	1.5
30 % elastomer – 10 % SGF - 60 % re-PET	30	5.3
30 % elastomer – 20 % SGF - 50 % re-PET	24	3.2
30 % elastomer – 30 % SGF - 40 % re-PET	28	0.6
40 % elastomer – 10 % SGF - 50 % re-PET	21	3.2
40 % elastomer – 20 % SGF - 40 % re-PET	18	4.4
50 % elastomer – 10 % SGF - 40 % re-PET	14	0.1

Table A.4.8 Flexural Strength Data for Set VII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Flexural Strength (MPa)	Stand. Dev.
Elvaloy PTW	53	4.5
Elvaloy 1224 AC	65	3.2
Lotryl 28 MA 07	52	4.3
Lotader AX 8840	74	5.0
Lotader AX 8900	38	1.2

Table A.4.9 Flexural Strength Data for Set VIII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Flexural Strength (MPa)	Stand. Dev.
Mixing Protocol 1	47	1.7
Mixing Protocol 2	51	2.8
Mixing Protocol 3	54	3.8
Original Mixing Protocol	38	1.2

A.5 Flexural Modulus Results For All Sets

Table A.5.1 Flexural Modulus Data for Set II

Composite	Flexural Modulus (MPa)	Stand. Dev.
10 % SGF – 90 % re-PET	3877	971.1
20 % SGF – 80 % re-PET	4229	712.5
30 % SGF – 70 % re-PET	4053	202.7
40 % SGF – 60 % re-PET	5579	582.5
50 % SGF – 50 % re-PET	6907	725.5

Table A.5.2 Flexural Modulus Data for Set III

Blend	Flexural Modulus (MPa)	Stand. Dev.
10 % elastomer – 90 % re-PET	1838	57.3
20 % elastomer – 80 % re-PET	834	211.1
30 % elastomer – 70 % re-PET	866	88.1
40 % elastomer – 60 % re-PET	565	21.0
50 % elastomer – 50 % re-PET	379	93.2

Table A.5.3 Flexural Modulus Data for Set IV (Effect of Screw Speed)

Composite	Flexural Modulus (MPa)	Stand. Dev.
30 % SGF – 70 % re-PET 170 rpm	4573	680.0
30 % SGF – 70 % re-PET 230 rpm	4653	202.7
30 % SGF – 70 % re-PET 290 rpm	4385	686.0

Table A.5.4 Flexural Modulus Data for Set IV (Effect of Temperature Profile)

Composite	Flexural Modulus (MPa)	Stand. Dev.
30 % SGF – 70 % re-PET 280 °C Die Temperature	4596	125.8
30 % SGF – 70 % re-PET 290 °C Die Temperature	4653	202.7
30 % SGF – 70 % re-PET 300 °C Die Temperature	4410	341.4

Table A.5.5 Flexural Modulus Data for Set V (Effect of Screw Speed)

Blend	Flexural Modulus (MPa)	Stand. Dev.
30 % elastomer – 70 % re-PET 170 rpm	886	11.8
30 % elastomer – 70 % re-PET 230 rpm	866	88.1
30 % elastomer – 70 % re-PET 290 rpm	1138	15.9

Table A.5.6 Flexural Modulus Data for Set V (Effect of Temperature Profile)

Blend	Flexural Modulus (MPa)	Stand. Dev.
30 % elastomer – 70 % re-PET 280 °C Die Temperature	884	67.8
30 % elastomer – 70 % re-PET 290 °C Die Temperature	866	88.1
30 % elastomer – 70 % re-PET 300 °C Die Temperature	884	145.7

Table A.5.7 Flexural Modulus Data for Set VI

Composite	Flexural Modulus (MPa)	Stand. Dev.
10 % elastomer – 10 % SGF - 80 % re-PET	921	78.2
10 % elastomer – 20 % SGF - 70 % re-PET	1184	65.2
10 % elastomer – 30 % SGF - 60 % re-PET	1341	45.3
10 % elastomer – 40 % SGF - 50 % re-PET	1566	80.6
20 % elastomer – 10 % SGF - 70 % re-PET	1114	48.7
20 % elastomer – 20 % SGF - 60 % re-PET	1284	32.3
20 % elastomer – 30 % SGF - 50 % re-PET	1757	111.2
20 % elastomer – 40 % SGF - 40 % re-PET	2515	325.6
30 % elastomer – 10 % SGF - 60 % re-PET	1258	152.3
30 % elastomer – 20 % SGF - 50 % re-PET	886	113.4
30 % elastomer – 30 % SGF - 40 % re-PET	1299	100.2
40 % elastomer – 10 % SGF - 50 % re-PET	1194	101.9
40 % elastomer – 20 % SGF - 40 % re-PET	483	111.0
50 % elastomer – 10 % SGF - 40 % re-PET	371	27.2

Table A.5.8 Flexural Modulus Data for Set VII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Flexural Modulus (MPa)	Stand. Dev.
Elvaloy PTW	1853	267.3
Elvaloy 1224 AC	1892	325.9
Lotryl 28 MA 07	1683	259.8
Lotader AX 8840	2786	39.5
Lotader AX 8900	1284	48.7

Table A.5.9 Flexural Modulus Data for Set VIII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Flexural Modulus (MPa)	Stand. Dev.
Mixing Protocol 1	1666	106.5
Mixing Protocol 2	1808	268.1
Mixing Protocol 3	2125	184.3
Original Mixing Protocol	1284	48.7

A.6 Impact Strength Results For All Sets

Table A.6.1 Impact Strength Data for Set II

Composite	Impact Strength (kJ/m^2)	Stand. Dev.
10 % SGF – 90 % re-PET	5.9	1.2
20 % SGF – 80 % re-PET	4.3	0.6
30 % SGF – 70 % re-PET	4.9	0.8
40 % SGF – 60 % re-PET	6.2	0.9
50 % SGF – 50 % re-PET	4.1	0.6

Table A.6.2 Impact Strength Data for Set III

Composite	Impact Strength (kJ/m^2)	Stand. Dev.
10 % elastomer – 90 % re-PET	9.1	3.4
20 % elastomer – 80 % re-PET	14.7	4.5
30 % elastomer – 70 % re-PET	No break (> 80)	---
40 % elastomer – 60 % re-PET	No break (> 80)	---
50 % elastomer – 50 % re-PET	No break (> 80)	---

Table A.6.3 Impact Strength Data for Set IV (Effect of Screw Speed)

Composite	Impact Strength (kJ/m^2)	Stand. Dev.
30 % SGF – 70 % re-PET 170 rpm	5.3	0.7
30 % SGF – 70 % re-PET 230 rpm	4.9	0.8
30 % SGF – 70 % re-PET 290 rpm	6.0	0.7

Table A.6.4 Impact Strength Data for Set IV (Effect of Temperature Profile)

Composite	Impact Strength (kJ/m^2)	Stand. Dev.
30 % SGF – 70 % re-PET 280 °C Die Temperature	5.1	0.6
30 % SGF – 70 % re-PET 290 °C Die Temperature	4.9	0.8
30 % SGF – 70 % re-PET 300 °C Die Temperature	5.5	0.7

Table A.6.5 Impact Strength Data for Set V (Effect of Screw Speed)

Blend	Impact Strength (kJ/m^2)	Stand. Dev.
30 % elastomer – 70 % re-PET 170 RPM	No break (> 80)	---
30 % elastomer – 70 % re-PET 230 RPM	No break (> 80)	---
30 % elastomer – 70 % re-PET 290 RPM	No break (> 80)	---

Table A.6.6 Impact Strength Data for Set V (Effect of Temperature Profile)

Blend	Impact Strength (kJ/m^2)	Stand. Dev.
30 % elastomer – 70 % re-PET 280 °C Die Temperature	No break (> 80)	---
30 % elastomer – 70 % re-PET 290 °C Die Temperature	No break (> 80)	---
30 % elastomer – 70 % re-PET 300 °C Die Temperature	No break (> 80)	---

Table A.6.7 Impact Strength Data for Set VI

Composite	Impact Strength (kJ/m^2)	Stand. Dev.
10 % elastomer – 10 % SGF - 80 % re-PET	4.0	0.5
10 % elastomer – 20 % SGF - 70 % re-PET	6.0	0.6
10 % elastomer – 30 % SGF - 60 % re-PET	6.2	0.5
10 % elastomer – 40 % SGF - 50 % re-PET	7.4	0.7
20 % elastomer – 10 % SGF - 70 % re-PET	11.7	2.6
20 % elastomer – 20 % SGF - 60 % re-PET	24.4	6.3
20 % elastomer – 30 % SGF - 50 % re-PET	12.4	3.3
20 % elastomer – 40 % SGF - 40 % re-PET	6.5	1.0
30 % elastomer – 10 % SGF - 60 % re-PET	43.1	3.8
30 % elastomer – 20 % SGF - 50 % re-PET	12.2	2.6
30 % elastomer – 30 % SGF - 40 % re-PET	15.7	1.3
40 % elastomer – 10 % SGF - 50 % re-PET	No break (> 80)	---
40 % elastomer – 20 % SGF - 40 % re-PET	No break (> 80)	---
50 % elastomer – 10 % SGF - 40 % re-PET	No break (> 80)	---

Table A.6.8 Impact Strength Data for Set VII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Impact Strength (kJ/m^2)	Stand. Dev.
Elvaloy PTW	66.2	8.9
Elvaloy 1224 AC	7.2	1.1
Lotryl 28 MA 07	9.0	2.1
Lotader AX 8840	47.1	22.8
Lotader AX 8900	24.4	6.3

Table A.6.9 Impact Strength Data for Set VIII

Composite 20 % elastomer – 20 % SGF – 60 % re-PET	Impact Strength (kJ/m^2)	Stand. Dev.
Mixing Protocol 1	15.4	8.4
Mixing Protocol 2	14.1	7.2
Mixing Protocol 3	5.9	1.0
Original Mixing Protocol	24.4	6.3

APPENDIX B

Table B.1 Fiber length distribution data

Samples	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
Fibre Length (μ)										
0-100	14	27	13	---	12	10	13	28	10	7
101-200	50	93	47	104	71	42	54	61	42	35
201-300	70	70	79	76	68	55	69	133	55	43
301-400	83	72	63	37	86	47	132	71	47	61
401-500	137	109	91	123	96	143	60	34	143	140
501-600	27	28	67	54	40	75	52	58	75	71
601-700	19	1	40	6	27	28	---	15	28	33
701-800	---	---	---	---	---	---	---	---	---	10
801-900	---	---	---	---	---	---	---	---	---	---
901-1000	---	---	---	---	---	---	---	---	---	---
Total Number of Fibers	400	400	400	400	400	400	400	400	400	400

$S_1 \Rightarrow$ 10 % elastomer – 10 % SGF – 80 % re-PET

$S_2 \Rightarrow$ 10 % elastomer – 40 % SGF – 50 % re-PET

$S_3 \Rightarrow$ 20 % elastomer – 10 % SGF – 70 % re-PET

$S_4 \Rightarrow$ 50 % elastomer – 10 % SGF – 40 % re-PET

$S_5 \Rightarrow$ 30 % SGF – 70 % re-PET (170 rpm)

S_6 ⇒ 30 % SGF – 70 % re-PET (230 rpm)

S_7 ⇒ 30 % SGF – 70 % re-PET (290 rpm)

S_8 ⇒ 30 % SGF – 70 % re-PET (280 °C Die Temperature)

S_9 ⇒ 30 % SGF – 70 % re-PET (290 °C Die Temperature)

S_{10} ⇒ 30 % SGF – 70 % re-PET (300 °C Die Temperature)

APPENDIX C

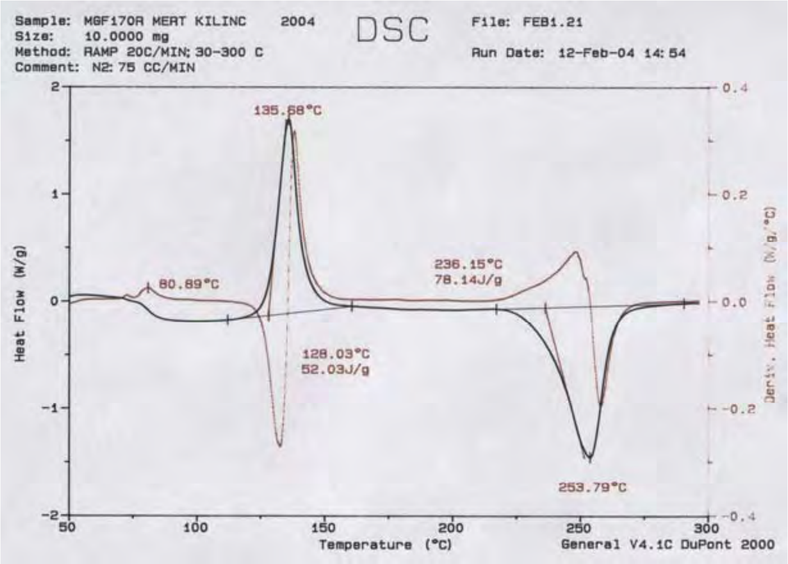

Figure C.1 DSC thermogram for effect of screw speed on glass fiber-rePET (170 RPM)

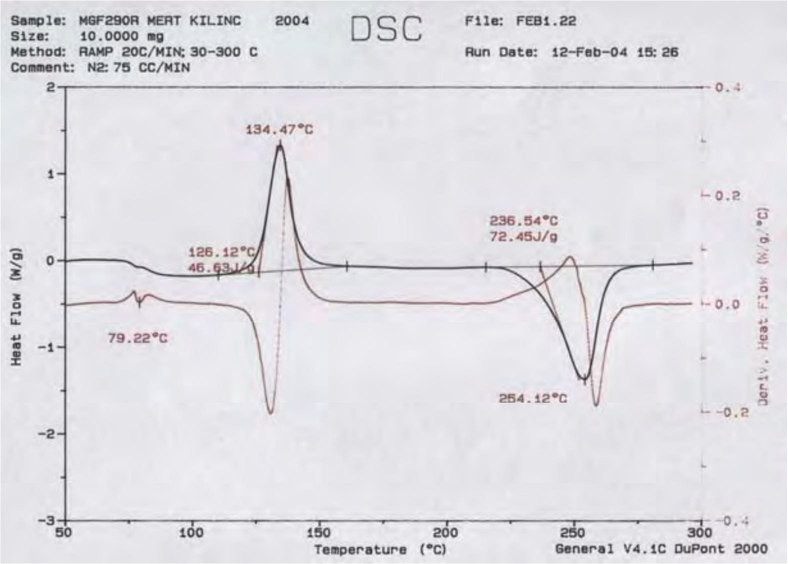

Figure C.2 DSC thermogram for effect of screw speed on glass fiber-rePET (290 RPM)

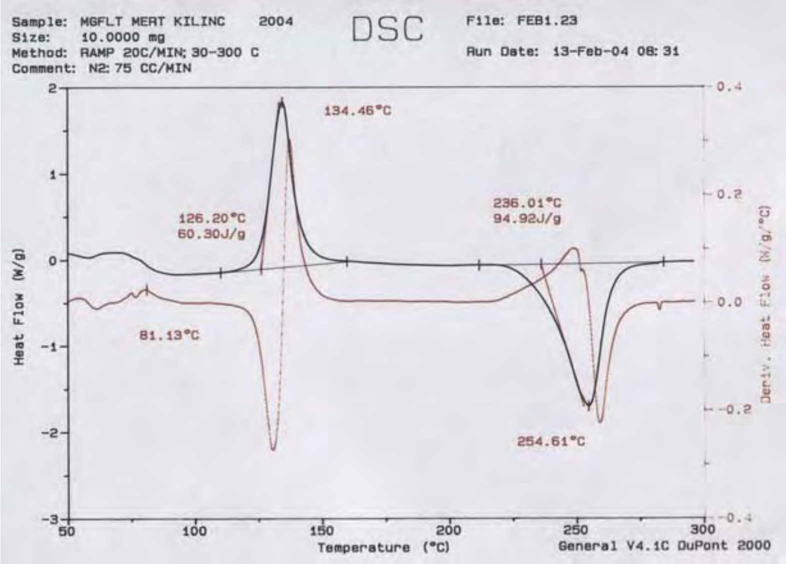

Figure C.3 DSC thermogram for effect of temperature profile on glass fiber-rePET (280 °C Die Temperature)

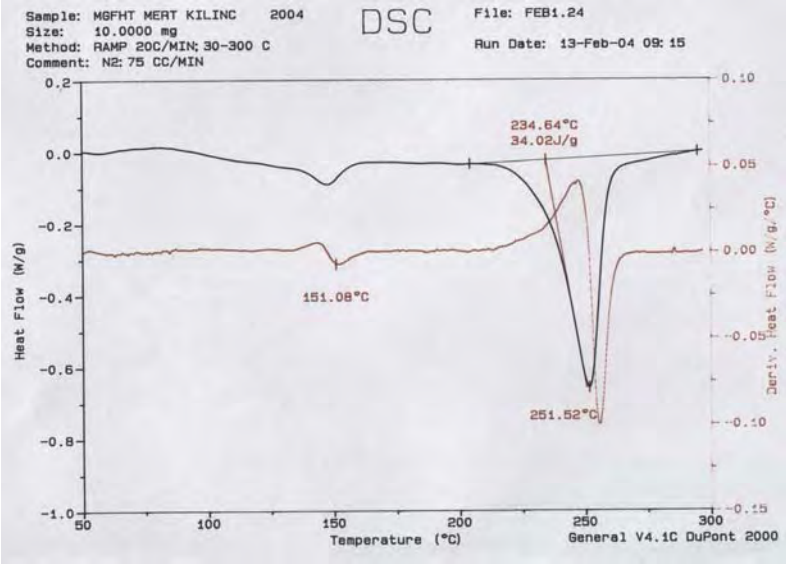

Figure C.4 DSC thermogram for effect of temperature profile on glass fiber-rePET (300 °C Die Temperature)

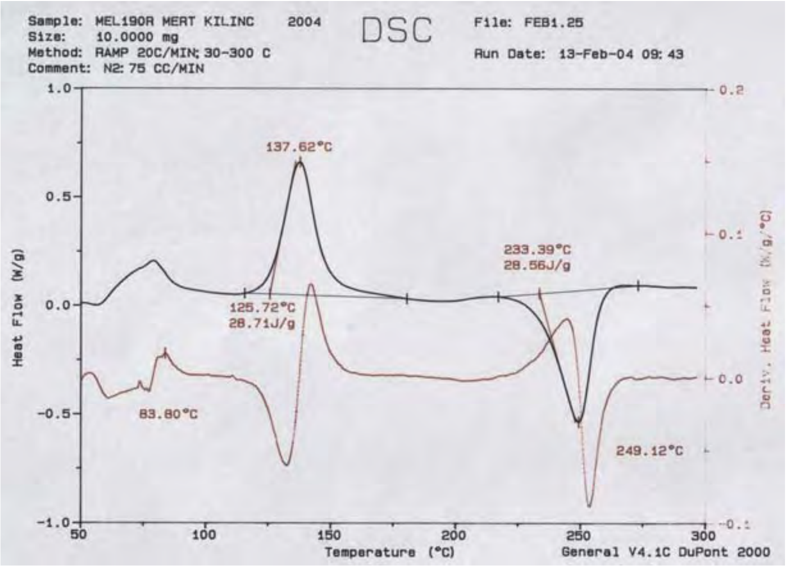

Figure C.5 DSC thermogram for effect of screw speed on elastomer-rePET (170 RPM)

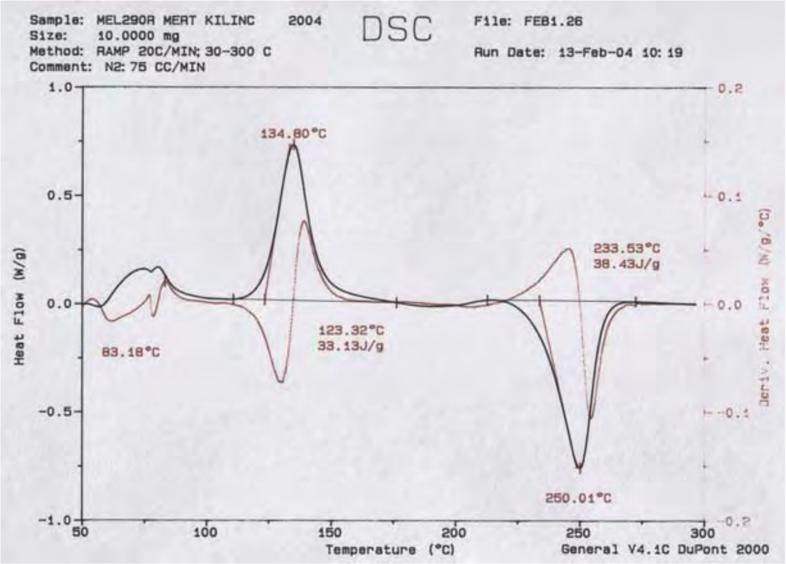

Figure C.6 DSC thermogram for effect of screw speed on elastomer-rePET (290 RPM)

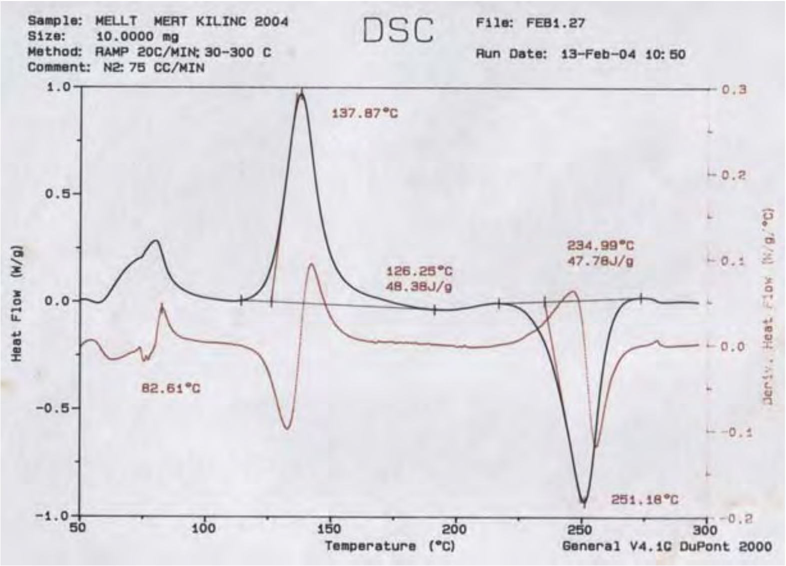

Figure C.7 DSC thermogram for effect of temperature profile on glass fiber-rePET (280 °C Die Temperature)

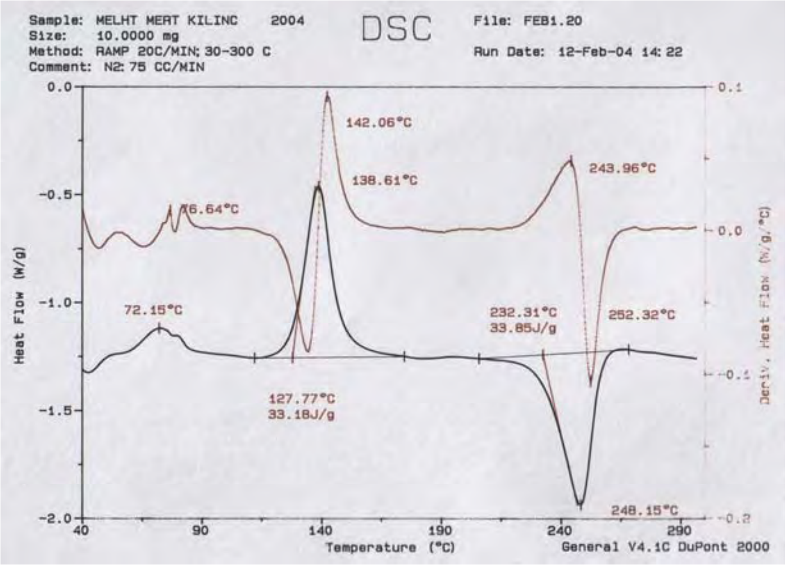

Figure C.8 DSC thermogram for effect of temperature profile on glass fiber-rePET (300 °C Die Temperature)

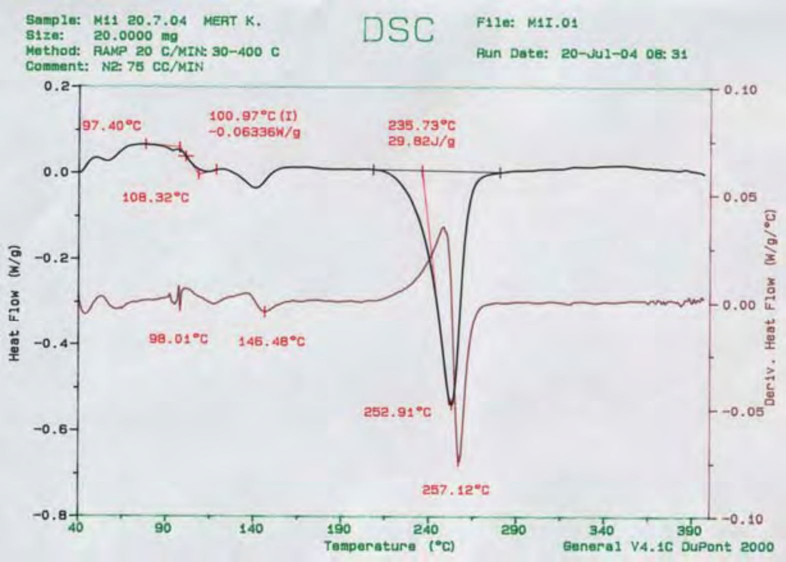

Figure C.9 DSC thermogram for 10 % elastomer – 10 % glass fiber – 80 % re-PET.

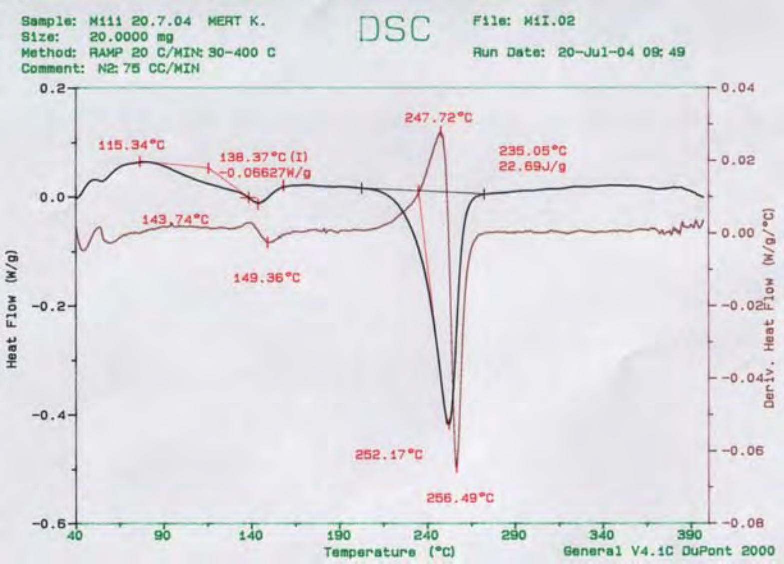

Figure C.10 DSC thermogram for 10 % elastomer – 20 % glass fiber – 70 % re-PET

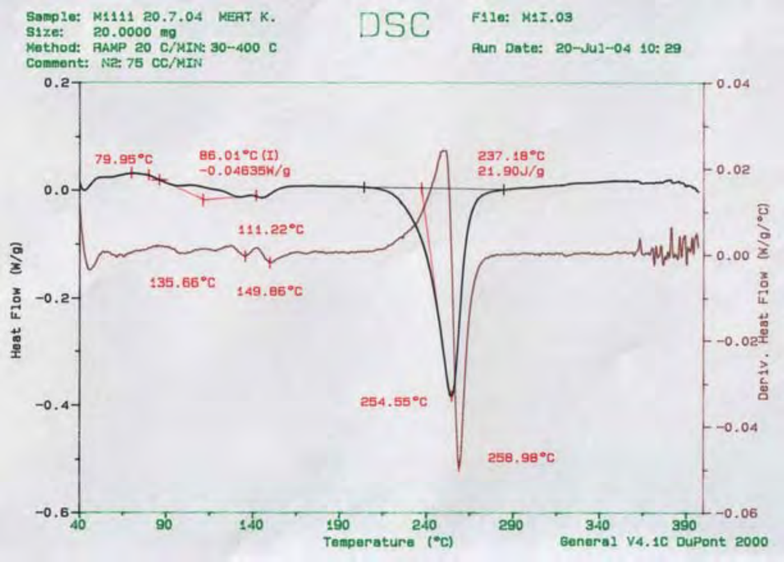

Figure C.11 DSC thermogram for 10 % elastomer – 30 % glass fiber – 60 % re-PET

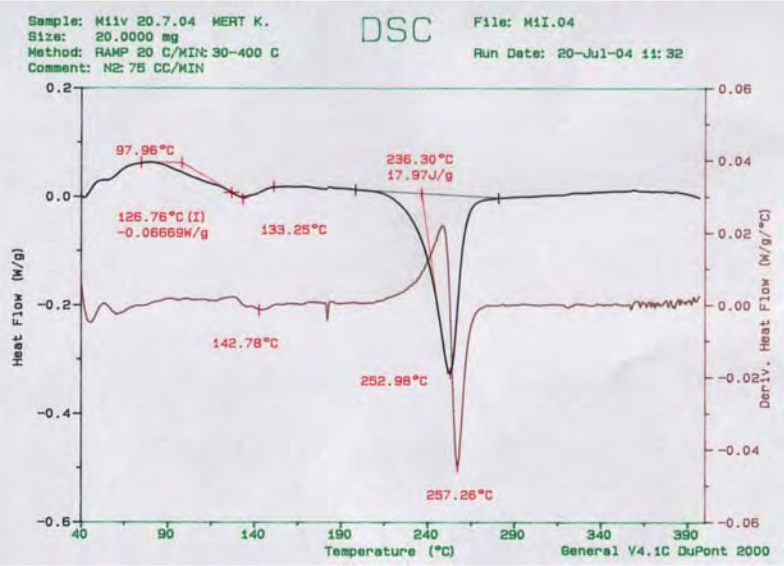

Figure C.12 DSC thermogram for 10 % elastomer – 40 % glass fiber – 50 % re-PET

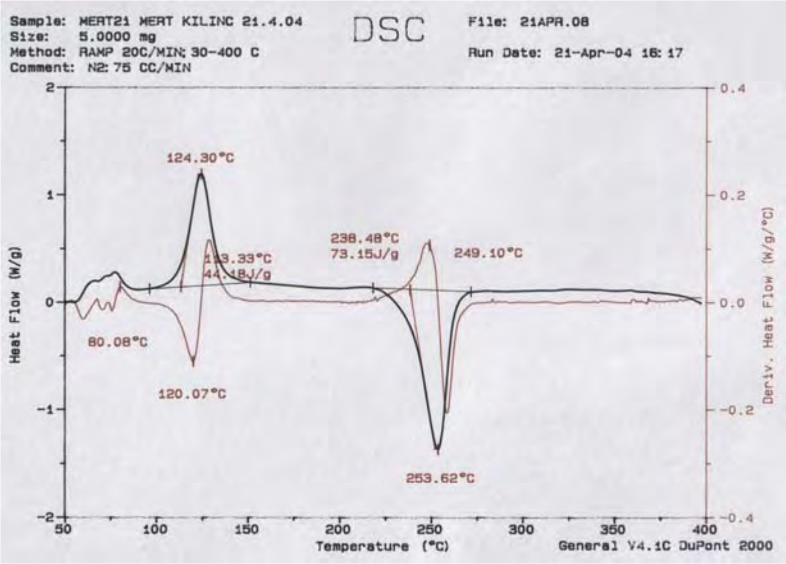

Figure C.13 DSC thermogram for 20 % elastomer – 10 % glass fiber – 70 % re-PET

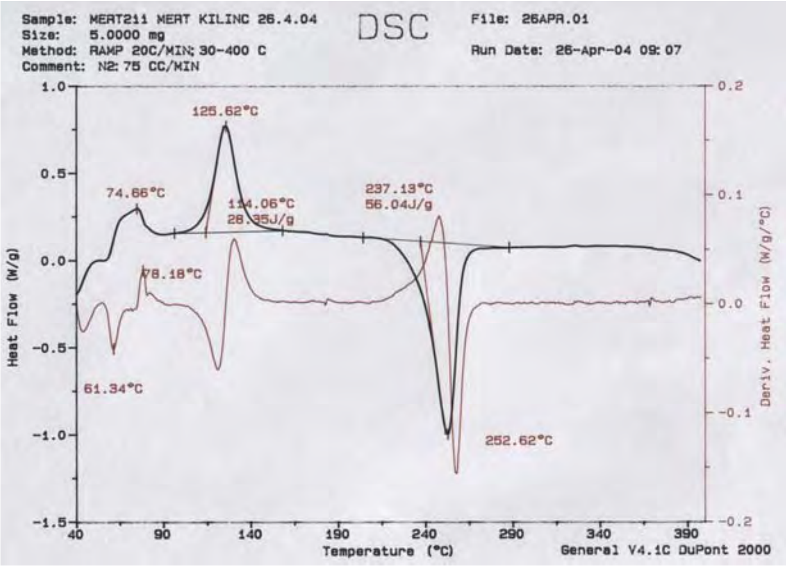

Figure C.14 DSC thermogram for 20 % elastomer – 20 % glass fiber – 60 % re-PET

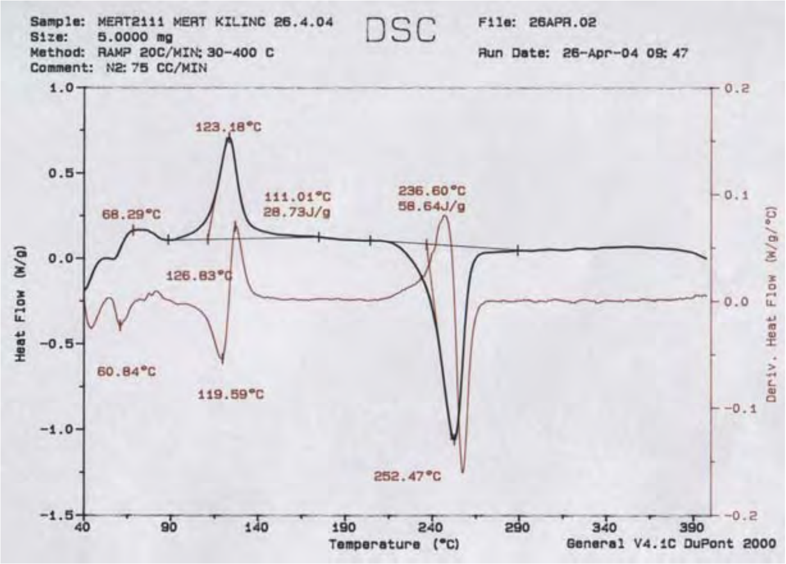

Figure C.15 DSC thermogram for 20 % elastomer – 30 % glass fiber – 50 % re-PET

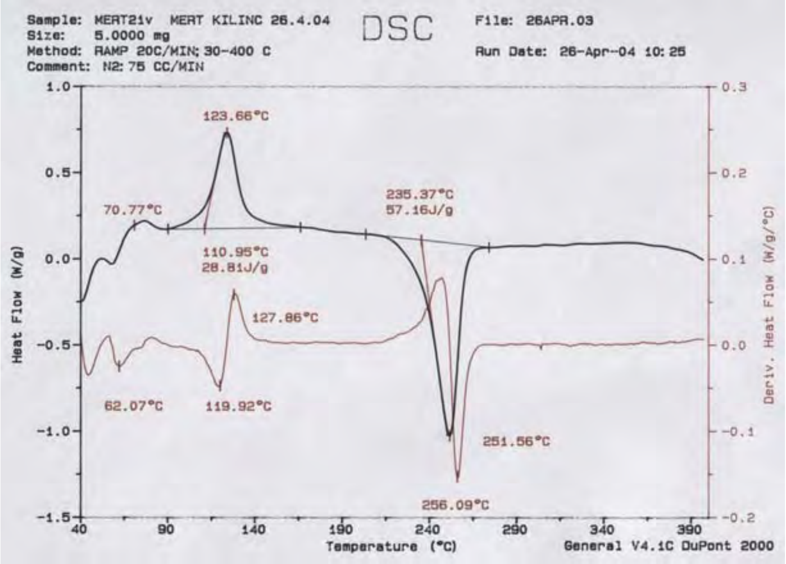

Figure C.16 DSC thermogram for 20 % elastomer – 40 % glass fiber – 40 % re-PET

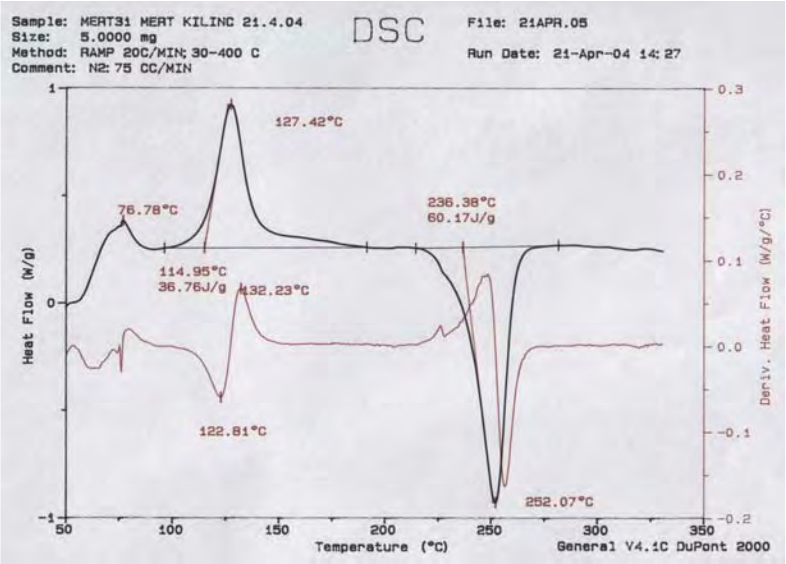

Figure C.17 DSC thermogram for 30 % elastomer – 10 % glass fiber – 60 % re-PET

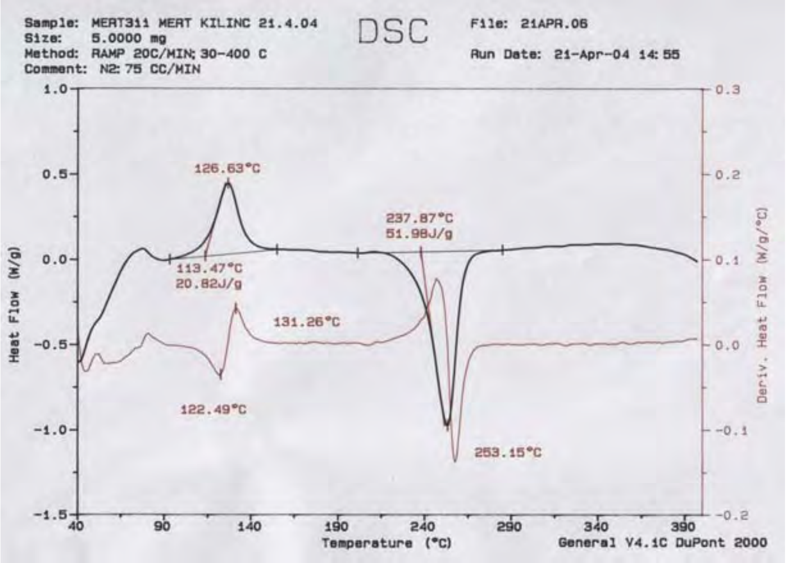

Figure C.18 DSC thermogram for 30 % elastomer – 10 % glass fiber – 60 % re-PET

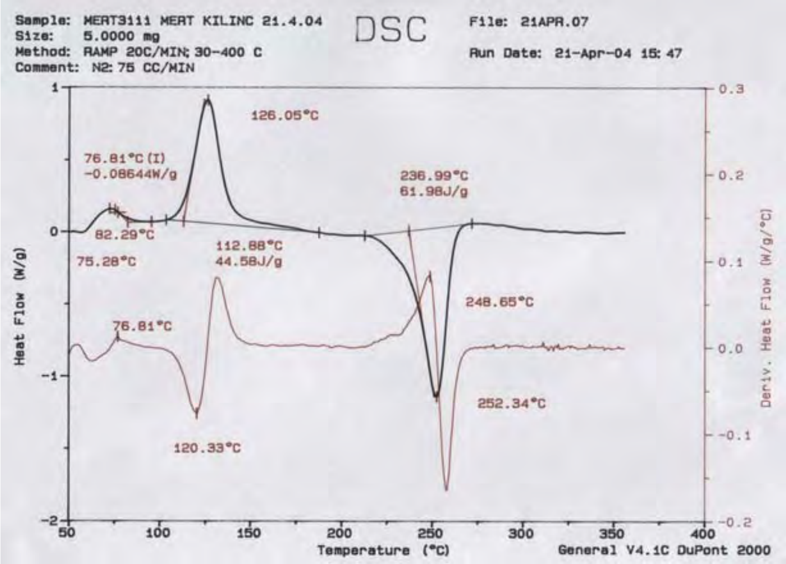

Figure C.19 DSC thermogram for 30 % elastomer – 30 % glass fiber – 40 % re-PET

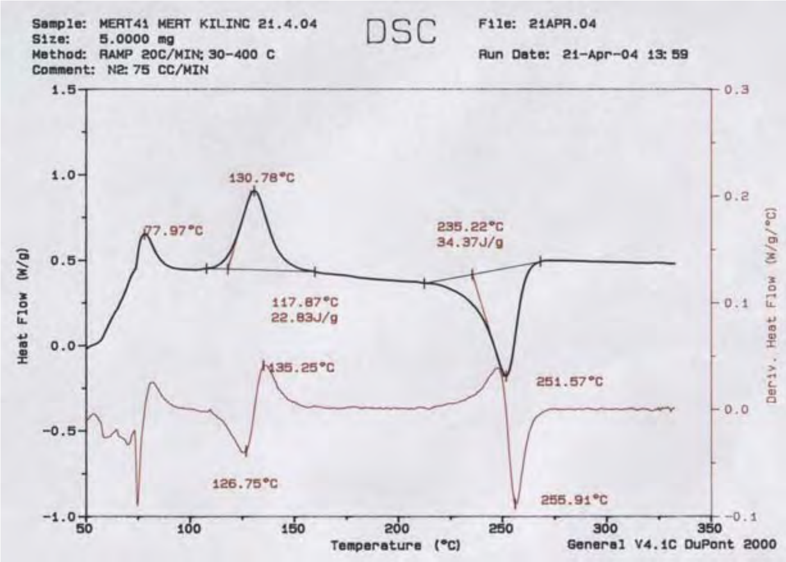

Figure C.20 DSC thermogram for 40 % elastomer – 10 % glass fiber – 50 % re-PET

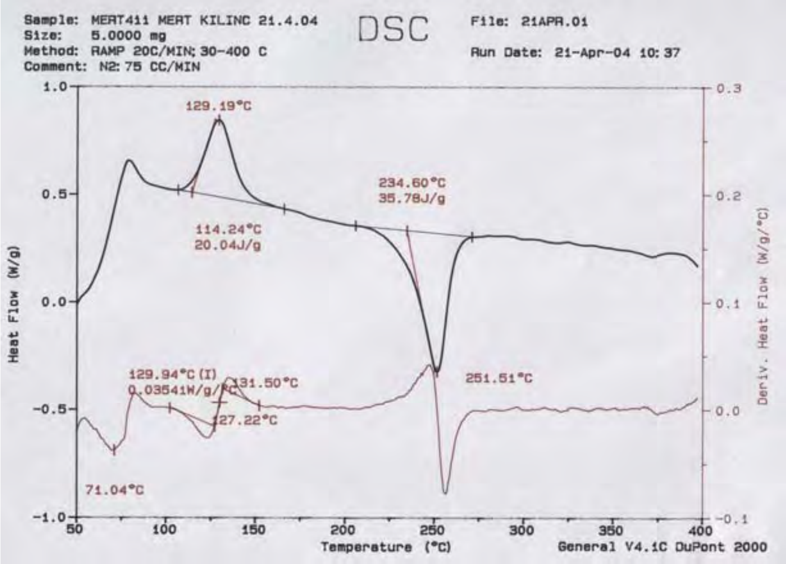

Figure C.21 DSC thermogram for 40 % elastomer – 20 % glass fiber – 40 % re-PET

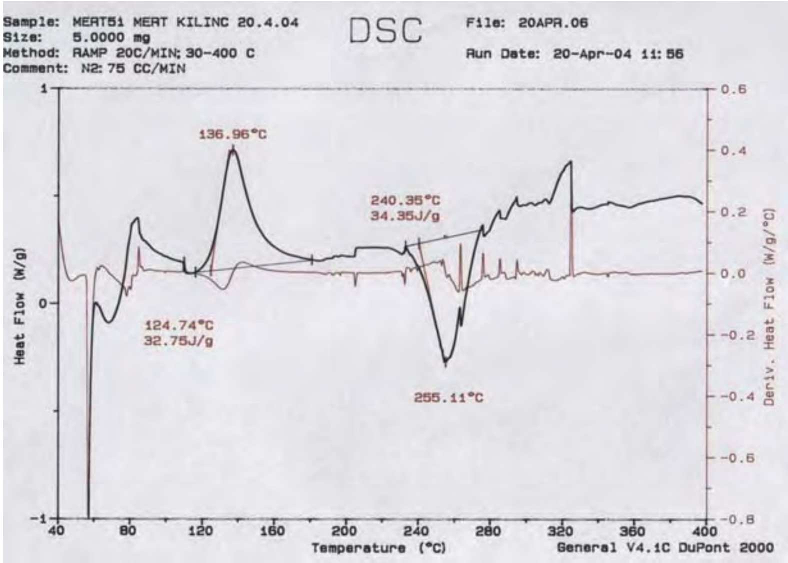

Figure C.22 DSC thermogram for 50 % elastomer – 10 % glass fiber – 40 % re-PET