# PREPARATION AND CHARACTERIZATION OF GLASS FIBER REINFORCED POLY(ETHYLENE TEREPHTHALATE)

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

CANSU ALTAN

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF
MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

JULY 2004

Approval of Graduate School of Natural and Applied Sciences

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# ABSTRACT

# PREPARATION AND CHARACTERIZATION OF GLASS FIBER REINFORCED POLY(ETHYLENE TEREPHTHALATE)

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July 2004, 123 pages

Glass fiber reinforced poly(ethylene terephthalate), GF/PET has excellent potential for future structural applications of composite materials. PET as a semi-crystalline thermoplastic polyester has high wear resistance, low coefficient of friction, high flexural modulus and superior dimensional stability make it a versatile material for designing mechanical and electromechanical parts.

Glass fibers are currently used as strength giving material in structural composites because of their high strength and high performance capabilities. In order to obtain high interfacial adhesion between glass fiber and polymer, glass fibers are treated with silane coupling agents.

The objective of this study is to produce GF/PET composites with varying glass fiber concentration at constant process parameters in a twin screw extruder. Also, by keeping GF content constant, it is aimed to observe the effects of process parameters such as screw speed and feed rate on structural properties of the composites. Another objective of the study is to investigate the influence of different coupling agents on the morphological, thermal and mechanical properties and on fiber length distributions of the composites.

Tensile strength and tensile moduli of the GF/PET composites increased with increasing GF loading. There was not a direct relation between strain at break values and GF content. The interfacial adhesion between glass fiber received from the manufacturer and PET was good as observed in the SEM photograps. Degree of crystallinity values increased with the addition of GF. Increasing the screw speed did not affect the tensile strength of the material significantly. While increasing the feed rate the tensile strength decreased. The coupling agent, 3-APME which has less effective functional groups than the others showed poor adhesion between glass fiber and PET. Therefore, lower tensile properties were obtained for the composite with 3-APME than those of other silane coupling agents treated composites. Number average fiber length values were reduced to approximately 300μm for almost all composites prepared in this study.

**Keywords:** Poly(ethylene terephthalate), Glass fiber, Silane Coupling Agents, Fiber length distribution, Extrusion, Compression Molding

# ÖZ

# CAM ELYAFLA GÜÇLENDİRİLMİŞ POLİ(ETİLEN TEREFTALAT) HAZIRLANMASI VE KARAKTERİZASYONU

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Cam elyafla güçlendirilmiş poli(etilen tereftalat), CE/PET, kompozit malzemelerin gelecekteki yapısal uygulamaları için mükemmel bir potansiyele sahiptir. Yarı-kristal bir termoplastik poliester olan PET'in aşınmaya karşı yüksek direnci, düşük sürtünme katsayısı, yüksek esneme modülü ve üstün ölçü stabilitesi; mekanik ve elektromekanik parçaların tasarımı için uygun bir malzeme olmasını sağlamaktadır.

Yüksek dayanımı ve yüksek performans sağlama yeteneği nedeniyle cam elyaf, yapısal kompozitlerde güçlendirici olarak kullanılırlar. Cam elyaf ve polimer iç yüzeyinde iyi bir yapışma elde edebilmek için, cam elyaf silan bağlayıcılarla muamele edilir.

Bu çalışmanın amacı, farklı cam elyaf miktarlarında, ekstrüderdeki sabit proses parametrelerinde CE/PET kompozitlerini üretmektir. Ayrıca, CE miktarını sabit tutarak, vida hızı ve besleme hızı gibi proses parametrelerinin kompozitlerin yapısal özellikleri üzerine olan etkisinin gözlenmesi amaçlanmaktadır. Çalışmanın bir başka amacı da değişik silan bağlayıcılarının, kompozitlerin morfolojik, termal ve mekanik özelliklerine ve elyaf uzunluk dağılımına olan etkilerini araştırmaktır.

CE miktarı arttıkça, cam elyaf/PET kompozitlerinin çekme dayanımı ve modülleri yükseldi. Kopmadaki uzama değerleri ve CE miktarı arasında direkt bir bağlantı gözlenmedi. Üreticiden alınan cam elyaf ile PET ara yüzeyi arasında iyi bir yapışma olduğu SEM fotoğraflarında gözlendi. CE eklenmesiyle kompozitlerin kristallenme dereceleri arttı. Artan vida hızı çekme dayanımını önemli ölçüde etkilemedi. Besleme hızı artarken çekme dayanımı azaldı. Diğer bağlayıcılara göre daha az etkili fonksiyonel gurubu olan 3-APME bağlayıcısı cam elyaf ve polimer arasındaki yapışmayı azalttı. Sonuç olarak, diğer silan bağlayıcılarla hazırlanan kompozitlerin çekme testi sonuçlarına göre, 3-APME içeren kompozitten daha düşük çekme özellikleri elde edildi. Bu çalışmada hazırlanan bütün kompozitlerde, sayısal ortalama elyaf boyu yaklaşık olarak 300μm değerine düştü.

**Anahtar Kelimeler:** Poli(etilen tereftalat), Cam Elyafı, Silan bağlayıcılar, Elyaf uzunluğu dağılımı, Ekstrüzyon, Baskı kalıplama

***To mum, dad and my sister Canipek…..***

# ACKNOWLEDGEMENTS

I present my sincerest thanks to my thesis supervisor, Assoc.Prof.Dr. Göknur Bayram for her great patience, understanding, guidance, encouragement and valuable discussions during this study.

I wish to express my sincere thanks to Prof.Dr. Ülkü Yılmazer for his valuable comments, Dr. Cevdet Öztin for his support, Cengiz Tan from Metallurgical and Materials Engineering Department for SEM analysis, Mihrican Açıkgöz from Chemical Engineering Department for DSC studies.

I would like to express my special thanks to Dr. Aref Javaherian and Sebahat Erdemli from Cam Elyaf Sanayi A.Ş. for their great help and support during my studies.

I extend my sincerest thanks to Zerrin Öğünç for her patience, understanding and encouragement, to Yalçın Çil and Işıl Işık for their peerless helps. I present special thanks to Mert Kılınç for his support during my experiments. Many thanks to my dear friends Çiğdem Başara, Güralp Özkoç and the members of Polymer Group for their help and friendship.

I wish to present sincere thanks to my family, Birsen, Metin and Canipek for their infinite confidence, great support and endless patience throughout this study. It would be impossible for me to finish this thesis without their love.

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| | |
|---|---|
| APET | Amorphous poly(ethylene terephthalate) |
| CPET | Crystalline poly(ethylene terephthalate) |
| RPET | Recycled poly(ethylene terephthalate) |
| 3-APME | 3-Aminopropylmethyldiethoxysilane |
| N-B-3-APM | N-(n-Butyl)-3-aminopropyltrimethoxysilane |
| 3-APE | 3-Aminopropyltriethoxysilane |
| 3-GPM | 3-Glycidoxypropyltrimethoxysilane |

# CHAPTER I

# INTRODUCTION

A composite is a combination of two or more components, usually made from polymers or polymers along with other kind of materials. The advantages such as, high stiffness, high strength, good corrosion and wear resistance and thermal stability make composites an important product in various industrial applications.

Poly(ethylene terephthalate), PET is widely used in synthetic fibers, film, bottling and composite production. Because of its excellent thermal stability, PET is also used as coating material for microwave and conventional ovens. Amorphous PET (APET) and crystalline PET (CPET) are two main types of PET. CPET has opaque structure, while APET provides glass quality clarity.

Polymer recycling has gained more importance because of the environmental effects. If the products save their property, recoverable materials can be recycled. Recycled PET is available for recycling methods, but degradation during proccesing must be considered.

Glass fibers (GF) are commonly used materials for the reinforcement of polymers such as thermoplastics. Because of their high strength, high performance capabilities, glass fibers are used as strength giving material in structural composites such as rocket motor cases, aircraft parts etc. The surfaces of glass fibers need to be treated by coupling agents in order to improve the interfacial adhesion between polymer and glass fiber. The most common coupling agents are silanes which have a specific formula, while one functional group reacts with surface of glass fiber, the other reacts with the functional group of polymer. In order to improve adhesion between glass fiber and polymer, the functional groups must be reactive enough. Thus, selection of coupling agents depends on performance of interfacial reactions between glass fiber-silane and silane-polymer. With increasing efficiency of stress transfer from polymer to fiber, mechanical performance is affected positively.

Amount of glass fiber in the composite is an important parameter in reinforcement of thermoplastics, which affects mechanical properties directly. As amount of glass fiber in the composite increases, it is expected that tensile strength and tensile modulus also increase. However, the amount of reinforcing agent is not only one effect, process parameters during composite production are as important as glass fiber content on final propertis of composites as well.

Various number of polymers and materials made from them are obtained through different types of processing methods. Extrusion is one of these methods which are used to form thermoplastic items as a desired product with a uniform cross-section or used to produce composite materials in pellet forms. The basic types of extruders are twin screw extruder and single screw extruder; they differ in type of material transport and velocity profile mainly. Good mixing, good heat transfer, large melting capacity are important advantages of twin screw extruder. Another type of processing method which is needed to produce a homogeneously shaped plastic is compression molding. This method is the least expensive and simplest of all polymer processing operations.

In this study, glass fiber/PET composite pellets were prepared by using a twin screw extruder, and the produced pellets were shaped by compression molding to be used in characterization experiments.

In order to observe the effect of glass fiber content, recycled PET was reinforced by chopped E-Glass fiber at constant processing parameters. Then, the effects of extrusion processing parameters such as screw speed and feed rate on structural properties of composites were studied. Finally, glass fibers were treated by using four different types of coupling agents. GF/PET composites, having a constant amount of glass fiber at chosen process parameters were produced and characterized to observe the effects of type of silane coupling agent on final properties of materials.

The interfacial surfaces obtained from tensile tests were observed using a scanning electron microscope (SEM). Differential Scanning Calorimeter was used to analyze the thermal behavior of the composites. The tensile properties of the GF/PET composites, i.e. tensile strength, tensile (Young’s) modulus and strain at break (% Elongation) values were evaluated. The effects of varying amounts of glass fiber, process parameters and different kinds of coupling agents on fiber length distribution and number average fiber length were also studied.

# CHAPTER II

# BACKGROUND INFORMATION

## 2.1 Polyesters

Polyesters are among the most important classes of polymers in use today. They are easily found materials in daily life and are used in different kinds of applications from drinking bottles and photographic film to shirts and fabrics, can be both plastic and fibers. Polyesters have hydrocarbon backbones which contain ester linkages, shown in Figure 2.1.

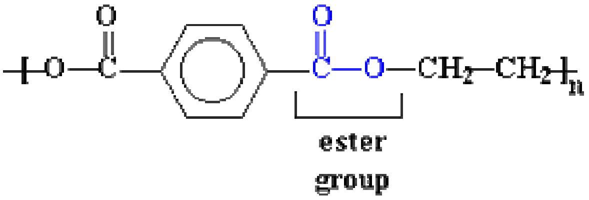


**Figure 2.1** Chemical structure of a polyester.

The ester groups in the polyester chain are polar with the carbonyl oxygen atom having a negative charge and the carbonyl carbon atom having a positive charge. The positive and negative charges of different ester groups are attracted to each other. This allows the ester groups of nearby chains to line with each other in crystal form, which is why they can form strong fibers. Commercially important polyesters are based on such polymers, of which poly(ethylene terephthalate) is the major product [1].

## 2.2 Poly(ethylene terephthalate), PET

PET is widely used in synthetic fibers, film, bottling and composite production. The glass transition temperature of PET is about 74°C. Crystallization of PET can be generally achieved upon heating to 190°C and orientation. Tranparency is achieved by rapid quenching. The production of poly(ethylene terephthalate) is conducted in two steps. Figure 2.2 shows the reactions of PET synthesis.

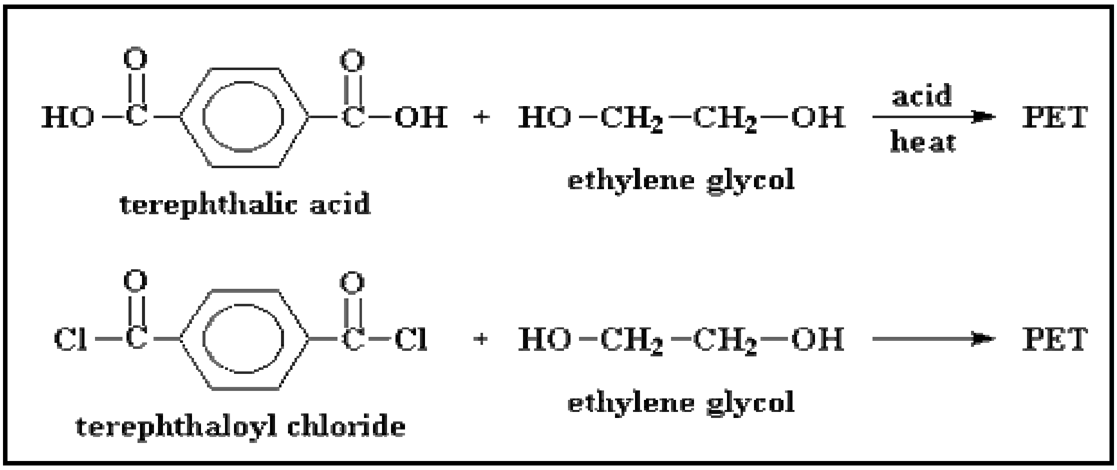


**Figure 2.2** Reactions of PET synthesis

Further heating to 270°C under vacuum in the presence of a catalyst produces the final polymer. Terephthalic acid is produced by air oxidation of p-xylene and ethylene glycol is obtained from ethylene oxide and water.

The strength of PET in its oriented form is outstanding. Oriented PET film is used in magnetic tape, x-ray and other photographic film applications, electrical insulation and food packaging. Production of PET bottles for carbonated beverages by blow molding has gained prominence because

PET has low permeability to carbondioxide and it can be easily recycled. Because of its excellent thermal stability, PET is also used as coating material for microwave and conventional ovens [2].

### 2.2.1 Types of PET

There are two main types of PET; Amorphous PET (APET) and Crystalline PET (CPET), the main difference being that, CPET is partially crystallized, while APET is amorphous. The partially crystalline structure of CPET makes it dimensionally stable at high temperatures. Due to this partially crystalline structure, CPET is opaque, while APET’s amorphous structure provides clarity of glass quality.

#### 2.2.1.1 Amorphous and Crystalline Structure

Crystallinity makes a material strong, but it also makes it brittle. A completely crystalline polymer would be too brittle to be used as plastic. The amorphous regions give a polymer toughness, that is, the ability to bend without breaking. Crystalline polymers have an amorphous part. This part usually makes up 40-70% of the polymer sample. This is why the same sample of a polymer can have both a glass transition temperature and a melting temperature. Figure 2.3 shows how the crystalline and amorphous parts are arranged.

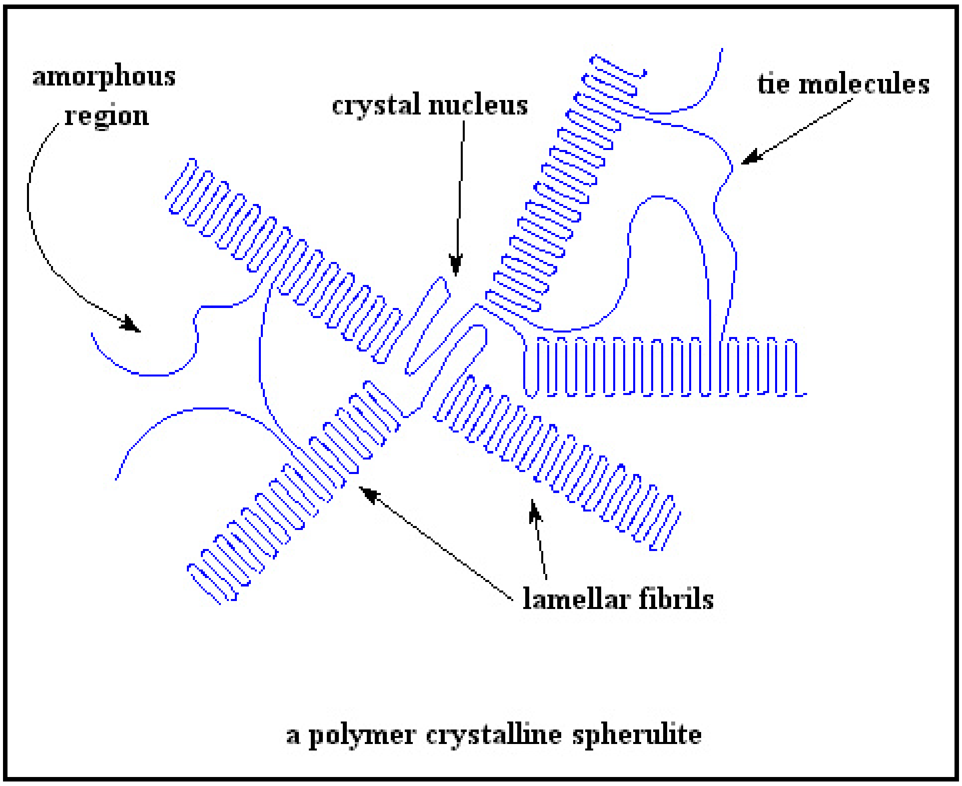


**Figure 2.3** Arrangement of crystalline and amorphous parts of a polymer

The crystalline part is in *lamellae*, where a stack of polymer chains folded back on themselves and the amorphous part is outside the lamellae. A single polymer chain may be partly in a crystalline lamella, and partly in amorphous state. These chains are called *tie molecules* [3].

#### 2.2.1.2 Glass Transition Temperature, $T_g$

Polymer chains are immobilized below $T_g$, while they are cooled rapidly through melting temperature, $T_m$, to below $T_g$, a metastable amorphous state in polymer can be obtained. When the polymer is annealed above $T_g$ and below $T_m$, it will crystallize, and the chains gain mobility. PET has important commercial applications in both amorphous state; soda bottles and in the crystalline state; textile fibers, microwaveable food trays, molding resin [4].

## 2.3 Recycled Poly(ethylene terephthalate)

Polyamides, polyesters, polycarbonate and polymethyl methacrylate are engineering plastics found in specific material streams (automative, electrical, PET bottles), which are relevant for recycling and have high quality in comparison with the other plastics. World consumption of PET in 1995 was 16.5 million tones. The United States used approximately 1.6 billion pounds of PET plastic packaging resins in 1993 and approximately 480 millions were being recycled. If the products save their properties, the recoverable materials can be recycled and data show that PET returnable bottle can be reused between 25 and 40 times. This indicates that mechanical and feedstock recycling methods are available for PET. Major sources of poly(ethylene terephthalate) for mechanical recycling are granules from the raw materials processing sector and from the post-consumer products sector, provided that they can be collected [5, 6].

Pawlak et al. [10] characterized the properties and composition of scrap PET from several sources. All PET samples they collected, contained mixture of other polymers (0.1-5 wt %). They found that molecular characteristic and properties of PET did not change, however the effects on mechanical properties came from admixtures and impurities.

The presence of more than 50 ppm PVC catalyzes the hydrolysis and reduces the strength of material. In addition to this, degradation during reprocessing influence mechanical properties of recycled PET negatively.

## 2.4 Reinforcing Agents

Plastics usually contain small amounts of one or more additives to improve the structural properties such as strength, stiffness, resistance to high temperatures. Reinforcing agents are the common additives which can be classified as glass fibers, carbon fibers, aramid fibers, etc. Short glass fibers are used widely to reinforce thermoplastics to give better dimensional control and stability and to increase strength of the plastic [4].

### 2.4.1 Glass Fibers

The appropriate ASTM standard (C167-71) defines glass, as “an inorganic product of fusion which has cooled to a rigid condition without crystallizing”. Because glass is amorphous, it is isotropic and has a glass transition point rather than melting point. Its tensile strength in fiber form is approximately 10 times more than in bulk form. Because of their high strength, high performance capabilities, glass fibers are used as strength giving material in structural composites such as rocket motor cases, pressure bottles and aircraft parts. There are several characteristics of glass fibers come from their nature which make them ideal reinforcements [9]. Here are some properties of glass fibers:

- *Superior Tensile Strength;* glass fibers have very high tensile strength.
- *Perfect Elasticity;* glass fibers obey Hooke's law. Typical glass fibers have a maximum elongation of 5% at break.
- *Attractive Thermal Properties;* they have low coefficient of thermal expansion and high thermal conductivity.
- *Excellent Moisture Resistance;* glass fibers do not absorb moisture.
- *Outstanding Dimensional Stability;* glass fibers do not shrink or stretch.
- *Excellent Corrosion Resistance;* they resist all organic solvents and most acids and alkalis.
- *Excellent Electrical Chracteristics;* glass fibers have high dielectric strengths and low dielectric constants.
- *Low Cost;* compared to other fibrous reinforcements, glass fibers have low cost [9].

#### 2.4.1.1 Glass Compositions

Glass compositions are classified due to the ingredients such as $SiO_2$, $Al_2O_3$, CaO and some other materials. Additionally, areas of uses determine the types of glass compositions. There are eight types of glass compositions;

*E-Glass;* is used for electric applications and it is the major product used as a reinforcement material for plastic composites.
*S-Glass;* is used for aerospace applications.
*D-Glass;* is used in random construction.
*A-Glass;* is used in window glass, bottles, containers.

*C-Glass;* is used in battery plate wrappers and chemical filters.
*L-Glass;* is used in radiation protection [9].

#### 2.4.1.2 E-Glass

The major part of all glass production today is E-glass. It is the first developed glass type for production of continuous fibers. This high tensile glass is the major product used as a reinforcement material for plastic composites. E-glass does not have a fixed composition but varies in composition as can be seen in Table 2.1 [9].

**Table 2.1** Composition of E-Glass

| **Components** | **Weight %** |
|---|---|
| $SiO_2$ | 52-56 |
| $Al_2O_3$ | 12-16 |
| CaO | 16-25 |
| MgO | 0-6 |
| $B_2O_3$ | 8-13 |
| $Na_2O$ and $K_2O$ | 0-3 |
| $TiO_2$ | 0-0.4 |
| $Fe_2O_3$ | 0.05-0.4 |
| $F_2$ | 0-0.5 |

Changes within the ranges of composition do not influence its mechanical properties [9].

## 2.5 Coupling Agents

Polymers have hydrophobic surfaces, while glass fibers have hydrophilic surfaces, that results poor interfacial adhesion. The use of glass fiber with untreated surface decreases strength properties of composites. Surface of glass fibers are treated by coupling agents in order to transfer stress from polymer to glass fiber. The most common coupling agents are silanes with the general formula of $Y\text{-}R\text{-}Si\text{-}(X)_3$. While X group reacts with the fiber surface, the Y group reacts with polymer. The use of silanes in thermoplastic/glass fiber composite systems improve the processing and strength properties and give environmental resistance to composites [4, 11].

### 2.5.1 Interfacial Reactions

The general structure of silane is shown in Figure 2.4, where X is a hydrolyzable group such as methoxy, ethoxy, acetoxy and Y is a organofunctional group attached to silicon by an alkyl bridge, R [11].

$$Y - R - Si - X_3$$

**Figure 2.4** General structure of silane

A reaction of a type of silane with water to the surface of glass fiber, which occurs in two rapid steps is shown in Figure 2.5. Firstly the silane ester hydrolyzes to the silane triol, and then condenses to the surface producing a chemically bonded or hydrogen bonded product. The double bonds then participate in the cure of an unsaturated polyester resin, covalently bonding the polymer to the surface [4, 11].

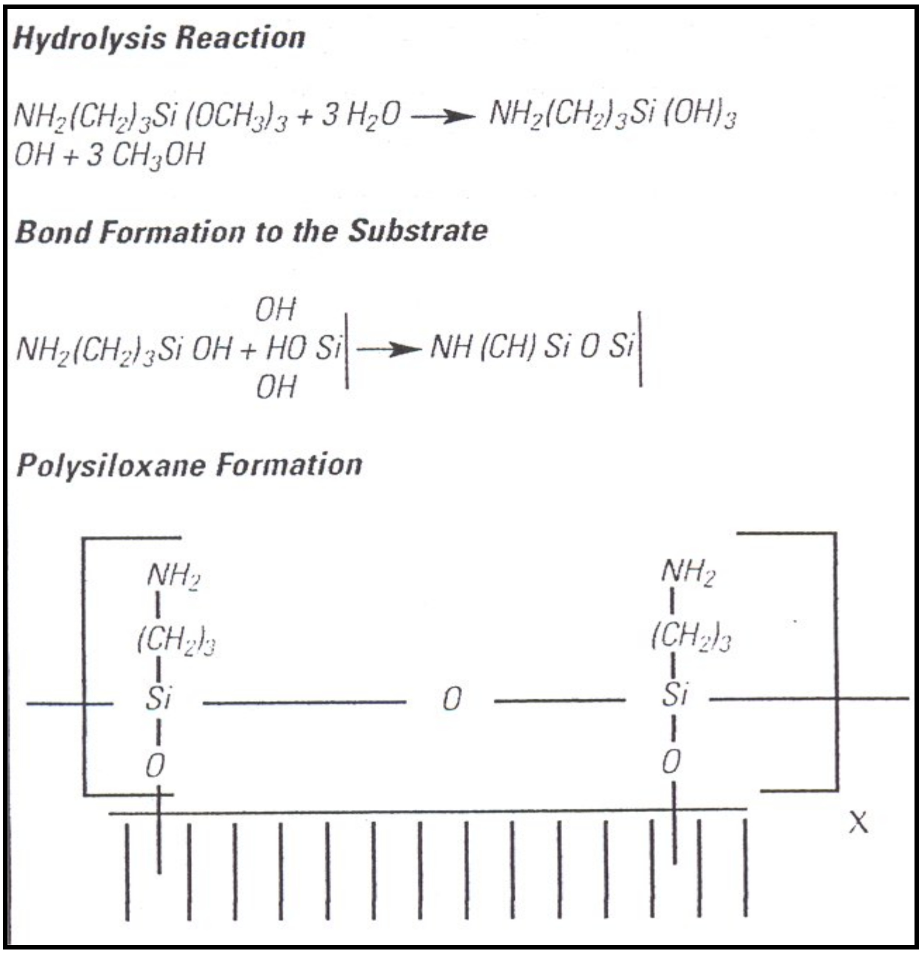


**Figure 2.5** Reaction of a type of silane with water to the surface of glass fiber

In order to improve adhesion between glass fiber and polymer, the functional groups must be reactive enough for the interfacial reaction to occur during extrusion. Figure 2.6 lists pairs of reactive groups commonly used in reactive blending and the covalent bonds accordingly formed [16].

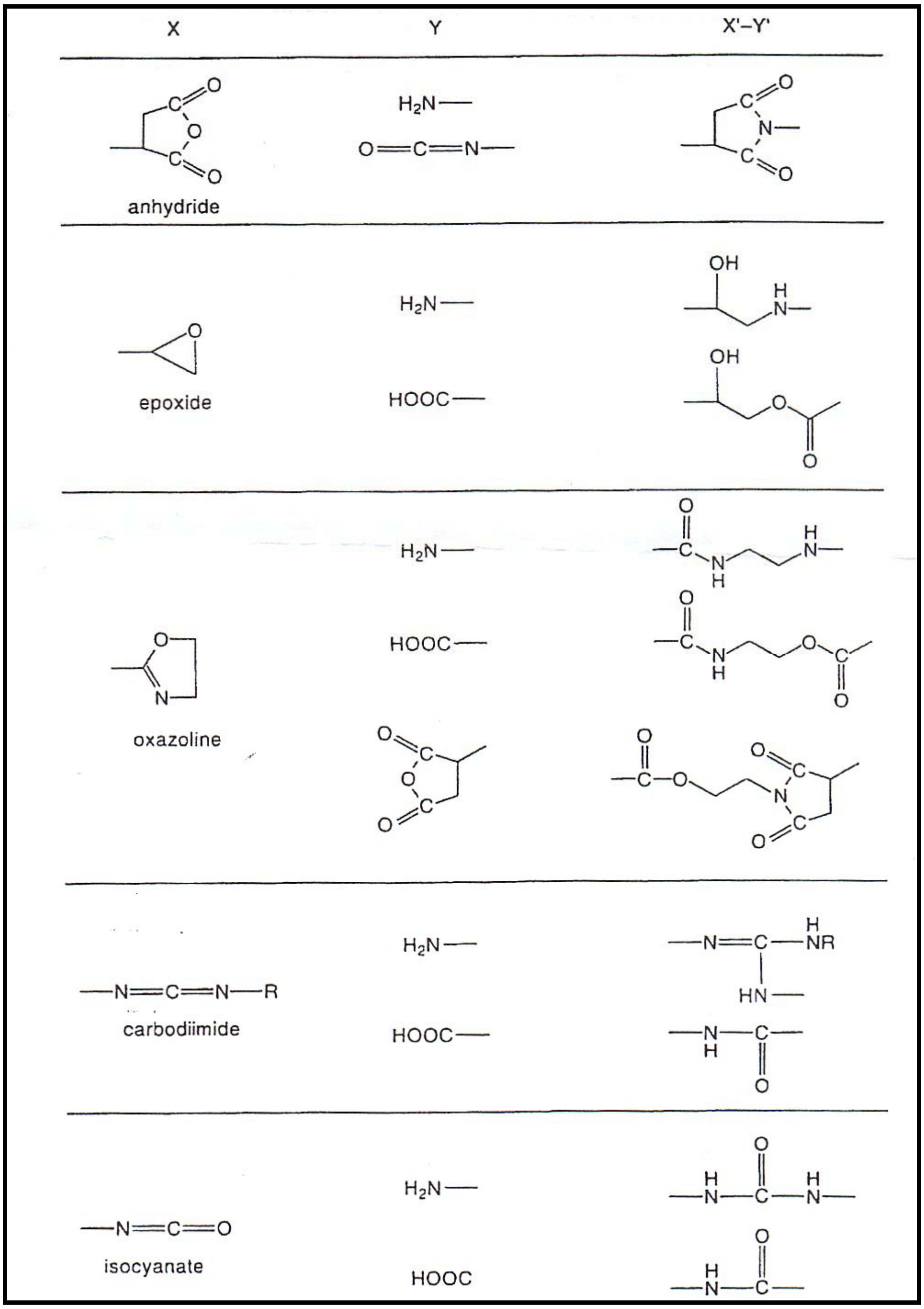


Figure 2.6 Reactive groups of interest for reactive blending

### 2.5.2 Surface Treatment Tecnique

There are three steps during surface treatment. Firstly, to obtain hydrolysis reaction, silan-water-alcohol mixture is prepared. Secondly, for dispersion of silane to the fiber a mechanical mixing is performed. Finally, to remove the by-products of the reaction and water or alcohol, heating is carried out. This method is usually used in thermoplastic, thermosetting and elastomeric resin systems. In the systems with water, deformation may occur in glass fiber integration and a partial decomposition of silane can be observed, however these problems can be reduced by using single alcohol solution [11].

Ihsak et al. [12] studied the effects of hygrothermal aging and a silane coupling agent on the tensile properties of injection molded short glass fiber reinforced poly(butylene terephthalate) composites. They used 3-aminopropyl-triethoxysilane (3-APE) as coupling agent. They diluted 3-APE in ethanol to make 20% solution with an amount of 3-APE to be the 2% by weight of short glass fiber. After the silane addition to the fiber they mixed the solution continuously for 30 minutes in order to obtain homogeneous dispersion of silane to the fiber surface. Then, they dried the treated fiber at 100°C for 5 hours in an air-circulating oven. As a result they observed the improvement of interfacial bonding between the fiber and thermoplastic. They explained that, mechanical performance is affected positively with increasing efficiency of stress transfer from polymer to fiber.

## 2.6 Composite Materials

A composite is any material made of more than one component, whose mechanical behavior and material properties are improved while they are used independently. Composites are made from polymers, or from polymers along with other kinds of materials such as glass fibers. The unique properties and various forms of glass fibers plus the variety of plastic materials give rise to glass-polymer combinations today. Composite materials have several advantages such as, high stiffness, high strength, good corrosion and wear resistance and thermal stability. Typical successful commercial and military applications of glass fiber reinforced plastics in various markets include [7, 9];

- transportation
- construction
- marine
- materials handling
- electrical
- sporting goods
- seating
- corrosion applications
- protective covers and housing
- appliance and equipment
- aerospace and military market

The composite production based on plastics, both thermosetting resins and thermoplastics is mainly fiber or filament, used either on its own or in mixtures. Non-fibrous materials, such as steel wire, can also be used. Additionally, surface-treated mineral fillers including mica platelets, talc, fibrous minerals, glass flakes are also used. The mechanical properties of the composite are largely determined by the type of reinforcement, its form and orientation. A high content of fibrous reinforcement produces a high tensile strength which increaes with the length of fiber, but does not confer high rigidity. A high mineral content may give high rigidity but relatively poor tensile strength. The balance between resin and reinforcement is the major factor which affects the properties of a composite structure. Fibrous materials act to reinforce matrix material by transferring the stress from polymer to fiber.

Polymers are commonly used as matrices, but, also other materials, such as metals, ceramics and cements are used as possible matrices for composite production [9].

## 2.7 Polymer Processing

Processing can be defined as the technology of converting raw polymer to materials in a desired shape. Variety of polymers and materials made from them are produced by using different processing methods, such as extrusion, calendering, fiber spinning, injection molding, compression molding, etc.

### 2.7.1 Extrusion

Extruder is a versatile machine which forms thermoplastic items with a uniform cross section such as pipe, hose and tubing, wire and cable, etc. Molding materials are conveyed down by a rotating screw which melt by proceeding down the barrel and forced through a die which gives it its final shape. Extruder screws are designed for the properties of polymer being extruded. Melting, compression and metering sections are basic sections of a screw. In melting part, the solid pellets are conveyed from the hopper and converted into molten polymer. In compression section, the molten polymer is compacted and mixed. The metering section is needed to produce the desired product cross section.

Twin screw extruder and single screw extruder are basic types of extruders. One of the fundamental difference between them is the type of transport that takes place in the extruder. While the material transports in a single screw extruder, it is a drag-induced type of transport. On the other hand, in a twin screw extruder, it is to extent a positive displacement type of transport. This means that, the frictional properties of materials can result feeding problems in a single screw extruder. The other important difference between these two types of extruders is the velocity profiles in the machine, which are well defined and easy to describe in single screw extruders, while they are more complicated in twin screw extruders. Good mixing, good heat transfer, large melting capacity, good devolatilization capacity and good control over stock temperatures can be described as the advantages of complex flow patterns [4, 13].

### 2.7.2 Compression Molding

Compression molding is a machine which has stationary and movable molds. The polymer is placed between them and then the mold is closed, heat and pressure are applied to obtain a homogeneously shaped plastic. Applied pressure and heat are dependent on the thermal and rheological properties of the polymer. A preheating time is needed to reduce holding time. Slow cooling or rapid cooling (quenching) can be applied at the end of holding time [1].

## 2.8 Characterization of Polymer-Glass Fiber Composites

Morphological, thermal and tensile tests can be performed in order to observe the effects of glass fiber content and silane coupling agents on PET. In addition, fiber length measurements can be experienced by using ignition test method and optical microscopy to examine the effects of process parameters on the fiber length.

### 2.8.1 Scanning Electron Microscopy (SEM) Analysis

SEM analyses are performed in order to observe the structure of material which is too small to observe using optical microscopy. The surface of material covered by a thin conducting film is scanned with a beam of electrons. The reflected beam of electrons is collected to provide the scanning on a cathode ray tube. The scanned surface can be analyzed on the screen in various magnifications [1].

### 2.8.2 Differential Scanning Calorimetry (DSC) Analysis

Thermal analysis of polymers can be performed in terms of, calorimetric and differential thermal analysis, thermo-gravimetric analysis, thermomechanical analysis, electrical thermal analysis and effluent gas analysis [1].

Differential scanning calorimetry is a technique to study thermal transitions of a polymer. Especially two pans sit on a pair of identically positioned platforms connected to a furnace by a common heat flow path. While putting the polymer sample in one pan, the other is the reference pan which is left empty. A design of DSC is shown in Figure 2.7.

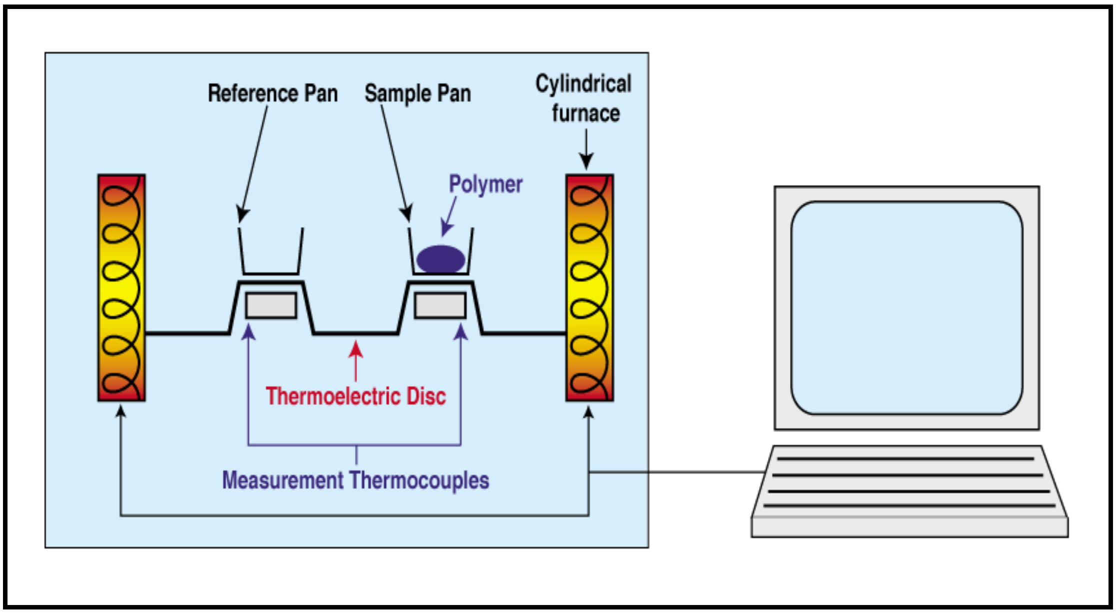


**Figure 2.7** Design of a DSC [3]

The two pans are heated at a specific rate, e.g. 20°C/min. Temperature and heat changes during DSC analysis are shown by plotting. As the temperature increases, on the x-axis the temperature is plotted and the difference in heat flow between the sample and reference is plotted on the y-axis. First, the plot will be constant with increasing temperature, after a certain temperature, the plot will shift downward suddenly which means that the polymer has gone through the glass transition. This helps to measure the glass transition temperature, $T_g$, of the sample. When the polymer show crystalline behavior it will give off heat and a big peak in the plot will occur. The temperature at the highest point is considered to be crystallization temperature, $T_c$, of the sample. Lastly, when the polymer reaches the melting temperature, a large dip will occur in DSC plot, which shows melting temperature, $T_m$. An example of a DSC plot is shown in Figure 2.8.

'% crystallinity' of a material can be calculated by using the formula given below.

$$\%crystallinity = \frac{\Delta H_m}{\Delta H_m^{\ o}} \times 100 \qquad (2.1)$$

where, $H_m$ is heat given off during melting and $\Delta H_m^o$ is specific heat of melting of 100% crystalline PET.

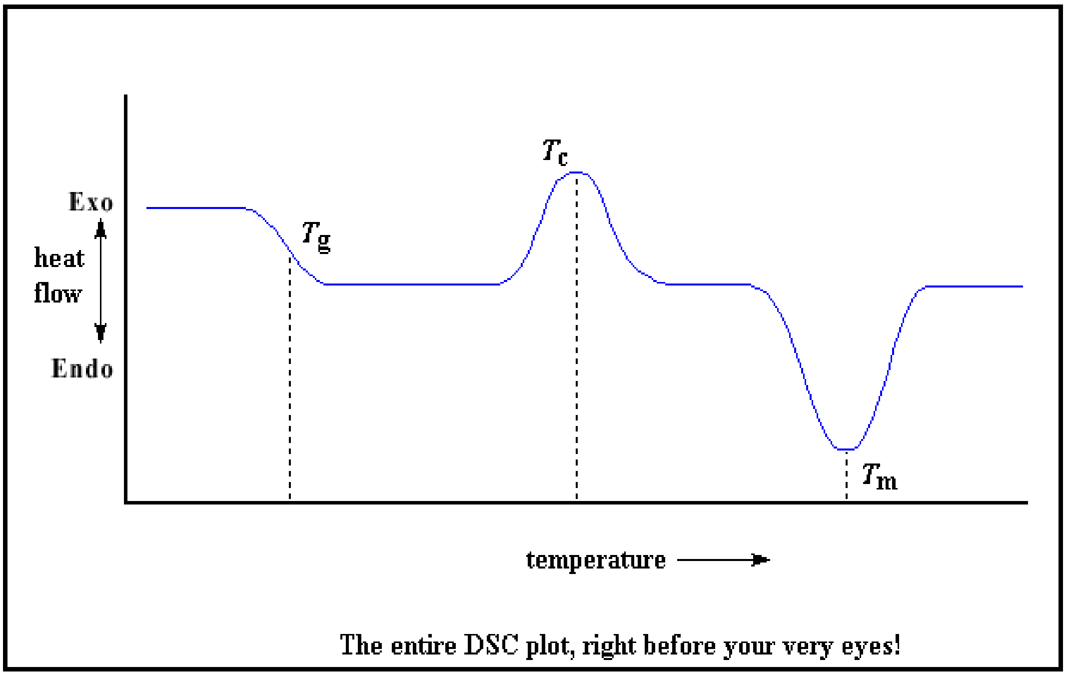


**Figure 2.8** A plot of DSC analysis [3]

### 2.8.3 Tensile Tests

Tensile tests are applied to observe the strength of produced material. A dog bone shaped specimen prepared according to ASTM standards is deformed with an increasing tensile load which is applied along the long axis of material at a constant rate. A stress versus strain graph is plotted, a drawing of which can be seen in Figure 2.9. While stretching the sample, the amount of force (F) applied is measured, and then by dividing the force by the cross-section area (A) of the sample, stress ($\sigma$ ) is obtained.

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

Strain, ($\varepsilon$), is defined according to equation below,

$$\varepsilon = \frac{\Delta L}{L_o} \qquad (2.3)$$

where;

$\Delta L$ = the change in gauge length of specimen
$L_o$ = initial gage length

Percent Elongation, (%E), is the extension at break by the original gage length, multiplied by 100.

$$\% Elongation = \frac{\Delta L}{L_o} \times 100 \qquad (2.4)$$

Tensile Modulus, (Young’s Modulus) is the ratio between stress and strain at break [14,15].

$$E = \frac{\sigma}{\varepsilon} \tag{2.5}$$

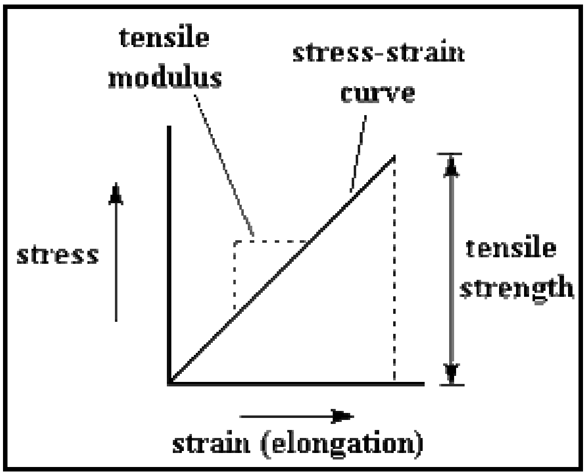


**Figure 2.9** A plot of stress-strain curve

### 2.8.4 Ignition Tests

Ignition tests can be used for different purposes, one of which is to obtain the amount of organic content of glass fibers such as coupling agents. The other is to determine the amount of GF in a reinforced thermoplastic. Then by using this information fiber length distribution and average fiber length can be obtained.

### 2.8.4.1 Organic Content Calculations

A constant amount of material contained in a curicible. At least three samples of curicible is ignited and allowed to burn until only ash remains. The ignition temperature is 565°C and holding time is 3 hours [15]. After ignition, remainings are cooled in a desicator and weighed. Weight percentage of organic material on the surface of glass fiber can be calculated according to the following equation:

$$weight\ \% = \frac{\Delta W}{W_i} x100 \tag{2.6}$$

where $\Delta W$ is the difference between the weights before and after ignition ($W_i$ – $W_f$) and $W_i$ is the initial weight of the sample.

### 2.8.4.2 Fiber Length Measurements

The same ignition test method explained above for 'organic content calculations' can be used, except 5 hours holding time in the furnace is applied [15]. Remained fibers are observed by using an optical microscope which sends the image to a screen. This provides measuring the fiber length distribution.

Weight average fiber length, $L_w$, and number average fiber length, $L_n$, can be calculated using the following equations [16]:

$$L_w = \frac{\sum N_t L_t^{\ 2}}{\sum N_t L_t} \tag{2.7}$$

$$L_n = \frac{\sum N_t L_t}{\sum N_t} \tag{2.8}$$

where $N_t$ is the number of fibers and $L_t$ is the length of fibers.

## 2.9 Previous Studies

Giraldi et al. [17] analyzed the effects of process parameters of twin screw extrusion on the mechanical properties of glass fiber/PET composites. They used 30% glass fiber and 0.5% antioxidant by weight. Injection molding method was used to prepare the specimens for mechanical tests. They used chopped glass fibers with an original length of 4.5mm and a diameter of 11μm. During processing, the screw speed was varied as 100 and 200rpm, screw torque values were 40 and 60%. The temperature profile used in the extruder was from 270 to 285°C. In the characterization part, they performed TGA, Intrinsic viscosity and MFI measurements, mechanical tests and fiber size distribution analysis. They found out that, for all sets of experiments the values of Izod impact strength and Young's modulus of composites increased when compared to those of unreinforced recycled PET. The higher screw torque (60%) increased the impact strength, while the higher screw speed (200rpm) increased the Young's modulus of the composites. Average fiber length distribution was found less than 1mm at the end of all sets of experiments.

Yılmazer and Cansever [18] studied the effects of processing conditions on fiber length distribution and mechanical properties of glass fiber reinforced Nylon-6. The composites were prepared by using a twin screw extruder at screw speeds of 250, 300 and 350rpm and feed rates of 70, 80 and 90kg/hr with a constant range of processing temperature. They used 30% glass fibers by weight with a length of 4.5mm for the reinforcement of polyamide. They found that as the screw speed was increased, weight average fiber length decreased. However a different behavior of fiber length distribution was observed with increasing feed rate. While the fiber length decreased in the feed rate range from 70 to 80kg/hr, an increase at the fiber length was observed between feed rate of 80 and 90kg/hr. As expected they found that as screw speed increased, tensile strength decreased with decreasing fiber length, however the highest value of modulus was seen at screw speed of 300rpm. When feed rate was increased from 70 to 80 g/min, tensile strength decreased and when it was increased from 80 to 90 g/min, an increase in tensile strength occurred.

Lee and Shin [19] produced glass fiber reinforced PET composite by a rapid press consolidation technique to observe the effects of vacuum, mold temperature and cooling rate on mechanical properties. Cooling rate affects the crystallinity of the composite. They used four different cooling methods such as, slow cooling ($1^oC$/min), normal A cooling ($10^oC$/min), normal B cooling ($20^oC$/min) and fast cooling ($100^oC$/min). They observed that, slow cooling rate affected the tensile strength positively in comparison with the other cooling rates. Additionally, the higher tensile modulus was obtained with slow cooling where the composite became more brittle. As expected, crystallinity decreased with increasing cooling rate.

Frenzel et al. [20] investigated the influence of glass fiber surface treatments on the morphology of PET and on the mechanical properties of glass fiber/PET composites. They treated E-glass fibers with coupling agent including aminosilane and they used polyurethane and epoxy resins as film formers. The amount of sizing applied to the glass fibers was 0.5-1.0 wt %. They produced the composite in the laminate form by compression molding, with a ratio of glass fiber to PET as 48:52 by volume. They found out that, glass fiber sizings did not change the crystallinity of PET significantly. The aminosilane coupling agent improved the mechanical properties of the composites. While epoxy resin increased the adhesion between glass fiber and PET, polyurethane did not influence the adhesion strength at the interphase.

Berg and Jones [21] examined the effects of sizing resins, coupling agents and their blends on the interphase in glass fiber composites by using an epoxy resin size with varying molecular weight, silanes at different coating thickness and blends of the silane and resin size. They used the fragmentation test in order to study the interfacial shear strength. They used E-glass fiber which were dip coated with a variety of coatings based on $\gamma$-aminopropyltriethoxysilane and epoxy resin sizing emulsions of three molecular weight, such as, low, medium and high. The low molecular weight size epoxy modified the properties of the two matrices, while the high molecular weight size reduced tensile strengths and affected interfacial shear strength negatively. Addition of silan reduced the interfacial shear strength of the high molecular epoxy sized fibers.

Park and Jin [22] applied $\gamma$-methacryloxypropyltrimethoxy silane containing $\gamma$-aminopropyltriethoxysilane to the surface of glass fibers with different concentrations in order to improve the interfacial adhesion at the interface between glass fiber and polyester. They observed an increase in surface free energy of the composites with the use of silane coupling agent compared with those as received. The mechanical interfacial properties of the composites decreased with higher silane coupling agent concentration, where the excess coupling agent formed a weak boundary layer and caused a lubrication effect.

Toth et al. [23] treated recycled PET by using epoxy-acrylate, 2% to the PET, as reactive additive and chopped glass fiber, 10-20% to the PET as reinforcement. They analyzed tensile, bending and impact resistance of the composites. They observed that the degradation in the recycled PET decreased tensile, bending and impact strength. The reactive additive did not affect mechanical properties independently, with the addition of 20% glass fiber the strength of PET incresed. They pointed out that the length of the short glass fibers is an important parameter to improve the adhesion between fiber and matrix. This means that the glass fibers shorter than a critical minimum length are pulled out from the matrix, if the adhesion between the fiber and the matrix is low.

Park et al. [24], studied the effects of silane coupling agent treatments on the glass fiber surface properties and the mechanical behavior of the glass fiber reinforced composities. They investigated the surface energies of the fibers and mechanical interfacial properties of the composities. They used $\gamma$-methacryloxypropytrimethoxy-silane (MPS), $\gamma$-aminopropyltriethoxysilane (APS) , and $\gamma$-glycidoxypropyltrimethoxy-silane (GPS) as coupling agents. They performed contact angle measurements in order to evaluate surface free energy between silane and fiber. Hydrogen bonding between the glass fiber and the silane coupling agent increased with the increase of hydroxyl groups which improved the degree of adhesion at the interfaces between glass fibers and coupling agents. The coupling agent, MPS having organic functional group which can react with the double bond of vinyl ester showed maximum surface free energy with respect to the others. With the presence of coupling agents they observed an increase in the adhesion at the interfaces among the glass fiber, the matrix and silane coupling agent. In order to observe the adhesion between glass fiber and polyester they performed SEM analysis and they found out that the silane treated glass fibers were coated with more polymer than untreated glass fibers.

# CHAPTER III

# EXPERIMENTAL

## 3.1 Materials

### 3.1.1 Poly(ethylene terephthalate)

Recycled poly(ethylene terephthalate), PET, which is in pellet form, was obtained from DuPontSA. It has some impurites such as PVC, glue, metal, etc. as also observed in the literature [10]. Some relevant properties of recycled PET which were obtained from DuPontSa are seen in Table 3.1.

**Table 3.1** Physical and tensile properties of recycled PET

| | |
|---|---|
| PVC | 60 ppm |
| Polyethylene | 5 ppm |
| Glue | 10 ppm |
| Paper | 3 ppm |
| $T_g$ (Glass Transition Temperature) | 60$^oC$ |
| $T_m$ (Melting Temperature) | 255 $^oC$ – 260 $^oC$ |
| Tensile Strength | 48 MPa |
| Tensile (Young's) Modulus | 2646 MPa |
| % Elongation | 2.58 % |

Recycled PET was processed by using a twin screw extruder and then, specimens for tensile tests were prepared by injection molding machine. Compression molding technique could not be used due to too brittle nature of recycled PET.

### 3.1.2 Glass Fiber

Glass fibers, GF, (PBT2) in clipped form were supplied by Cam Elyaf Sanayii A.Ş. Bunches of PBT2 type glass fiber are produced from E-Glass Fiber by extrusion for reinforcement of poly(butylene terephthalate), PBT, and PET. Its silane based coupling agent is suitable for PBT and PET resines. It has high integration, easy flow and good mechanical strength properties. Some material properties of glass fiber which were obtained from Cam Elyaf Sanayii A.Ş. are given in Table 3.2. This glass fiber as received was used to study the effects of glass fiber content and effects of processing parameters on structural properties of the composites.

**Table 3.2** Material properties of Glass Fiber

| | |
|---|---|
| Glass type | E-Glass |
| Fiber Length | 4.5 mm |
| Filament Diameter | Nom. 10.5µ |
| Humidity | Max. 0.07 |
| Size Type | Silane, (3-APE) |
| Size Amount | 0.75±0.20 % |
| Flow Character | Very Good |
| Resin Compatibility | PBT & PET |

### 3.1.3 Coupling Agents

Silane based coupling agents in liquid form were supplied by Cam Elyaf Sanayii A.Ş. Four kinds of coupling agents were used for fiber treatment purposes.

#### 3.1.3.1 3-Aminopropylmethyldiethoxysilane, 3-APME

It is an amino-functional silane which acts as an adhesion promoter between inorganic materials (glass, metals, fillers) and organic polymers (thermosets, thermoplastics and elastomers) and as a surface modifier. Figure 3.1 shows the chemical structure of this coupling agent.

$$H_2N\text{-}(CH_2)_3\text{-}Si(CH_3)(OC_2H_5)_2$$

**Figure 3.1** Chemical structure of 3-Aminopropylmethyldiethoxysilane

Physical properties of 3-Aminopropylmethyldiethoxysilane which were obtained from Cam Elyaf Sanayii A.Ş. are shown in Table 3.3.

**Table 3.3** Physical properties of 3-Aminopropylmethyldiethoxysilane

| | |
|---|---|
| Density (20$^o$C) | Approx. 0.92 g/cm$^3$ |
| Viscosity (20$^o$C) | Approx. 2 mPa.s |
| Boiling Point (1 atm) | Approx. 202 $^o$C |
| Flash Point | Approx. 85$^o$C |

### 3.1.3.2 N-(n-Butyl)-3-aminopropyltrimethoxysilane, N-B-3APM

It is a bifunctional silane possessing a reactive secondary amine and hydrozable methoxysilyl groups. The dual nature of its reactivity allows to bind chemically to both inorganic materials (glass, metals, fillers) and organic polymers (thermosets, thermoplastics, elastomers). Figure 3.2 shows the chemical structure of this coupling agent.

$$H_3C\text{-}(CH_2)_3\text{-}NH\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$$

**Figure 3.2** Chemical structure of N-(n-Butyl)-3-aminopropyltrimethoxysilane

Some significant physical properties of N-(n-Butyl)-3-aminopropyltrimethoxysilane which were obtained from Cam Elyaf Sanayii A.Ş. are shown in Table 3.4.

**Table 3.4** Physical properties of N-(n-Butyl)-3-aminopropyltrimethoxysilane

| | |
|---|---|
| Density (20$^o$C) | Approx. 0.95 g/cm$^3$ |
| pH (20$^o$C), 1:1 $H_2O$ | Approx. 11 |
| Viscosity (20$^o$C) | Approx. 2.5 mPa.s |
| Boiling Point (1 atm) | Approx. 238 $^o$C |
| Flash Point | Approx. 110 $^o$C |

#### 3.1.3.3 3-Aminopropyltriethoxysilane, 3-APE

It is a bifunctional silane possessing a reactive primary amino group and hydrolyzable ethoxysilyl groups. Figure 3.3 shows the chemical structure of this coupling agent.

$$H_2N\text{-}(CH_2)_3\text{-}Si(OC_2H_5)_3$$

**Figure 3.3** Chemical structure of 3-Aminopropyltriethoxysilane

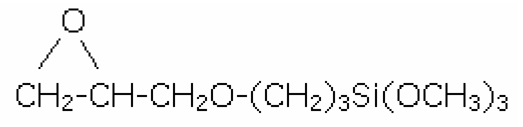
Physical properties of 3-Aminopropyltriethoxysilane which were obtained from Cam Elyaf Sanayii A.Ş. are given in Table 3.5.

**Table 3.5** Physical properties of 3-Aminopropyltriethoxysilane

| | |
|---|---|
| Density (20$^o$C) | Approx. 0.95 g/cm$^3$ |
| Viscosity (20$^o$C) | Approx. 1.85 mPa.s |
| Boiling Point (1 atm) | Approx. >68 $^o$C |
| Flash Point | Approx. 93 $^o$C |

#### 3.1.3.4 3-Glycidyloxypropyltrimethoxysilane, 3-GPM

It is a bifunctional organosilane possessing a reactive organic epoxide and hydrolyzable inorganic methoxysilyl groups. Figure 3.4 illustrates the chemical structure of this coupling agent.



$CH_2-CH-CH_2O-(CH_2)_3Si(OCH_3)_3$

**Figure 3.4** Chemical structure of 3-Glycidyloxypropyltrimethoxysilane

Physical properties for the 3-Glycidyloxypropyltrimethoxysilane which were obtained from Cam Elyaf Sanayii A.Ş. are shown in Table 3.6.

**Table 3.6** Physical properties of 3-Glycidyloxypropyltrimethoxysilane

| | |
|---|---|
| Density (20°C) | Approx. 1.07 g/cm$^3$ |
| Ignition temperature | Approx. 400 °C |
| Viscosity (20°C) | Approx. 3.7 mPa.s |
| Boiling Point (0.7 hPa) | Approx. 90 °C |
| Flash Point | Approx. 122 °C |

### 3.2 Fiber Treatment

All four coupling agents are soluble in alcohols and aliphatic or aromatic hydrocarbons. Coupling agents were diluted in methanol to make 20% solution. Because of the different bonding property of coupling agents to the glass fiber surface, solutions were prepared with different amounts of coupling agents. 1% by weight of bonded coupling agent was taken as basis. According to this, 3-Aminopropylmethyldiethoxysilane and 3-Aminopropyltriethoxysilane were used 5 grams, N-(n-butyl)-3-aminopropyltrimethoxysilane was taken as 4 grams and 3-Glycidyloxypropyltrimethoxysilane was used as 2.5 grams. 200 grams of glass fiber were used for each coupling agent. After addition of coupling agent solution into the fiber, the mixture was continuously mixed for 15 minutes at room temperature. The treated fiber was then dried for about 5 hours in an oven to allow complete evaporation of methanol. At this point the drying temperature is an important detail because of the different boiling point temperatures of coupling agents. 3-Aminopropylmethyldiethoxysilane and N-(n-butyl)-3-aminopropyltrimethoxysilane treated fiber were dried at 100°C, 3-Aminopropyltriethoxysilane and 3-Glycidyloxypropyltrimethoxysilane treated fibers were dried at 70°C. Ignition tests were performed to obtain the amount of bonded coupling agents. Figure 3.5 and 3.6 illustrate the experimental set-up and flowchart of the procedure for fiber treatment.

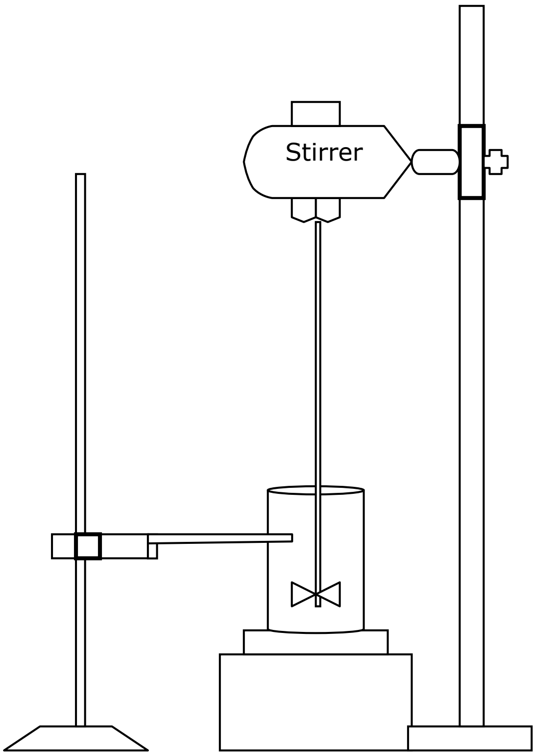


**Figure 3.5** Experimental set-up for fiber treatment

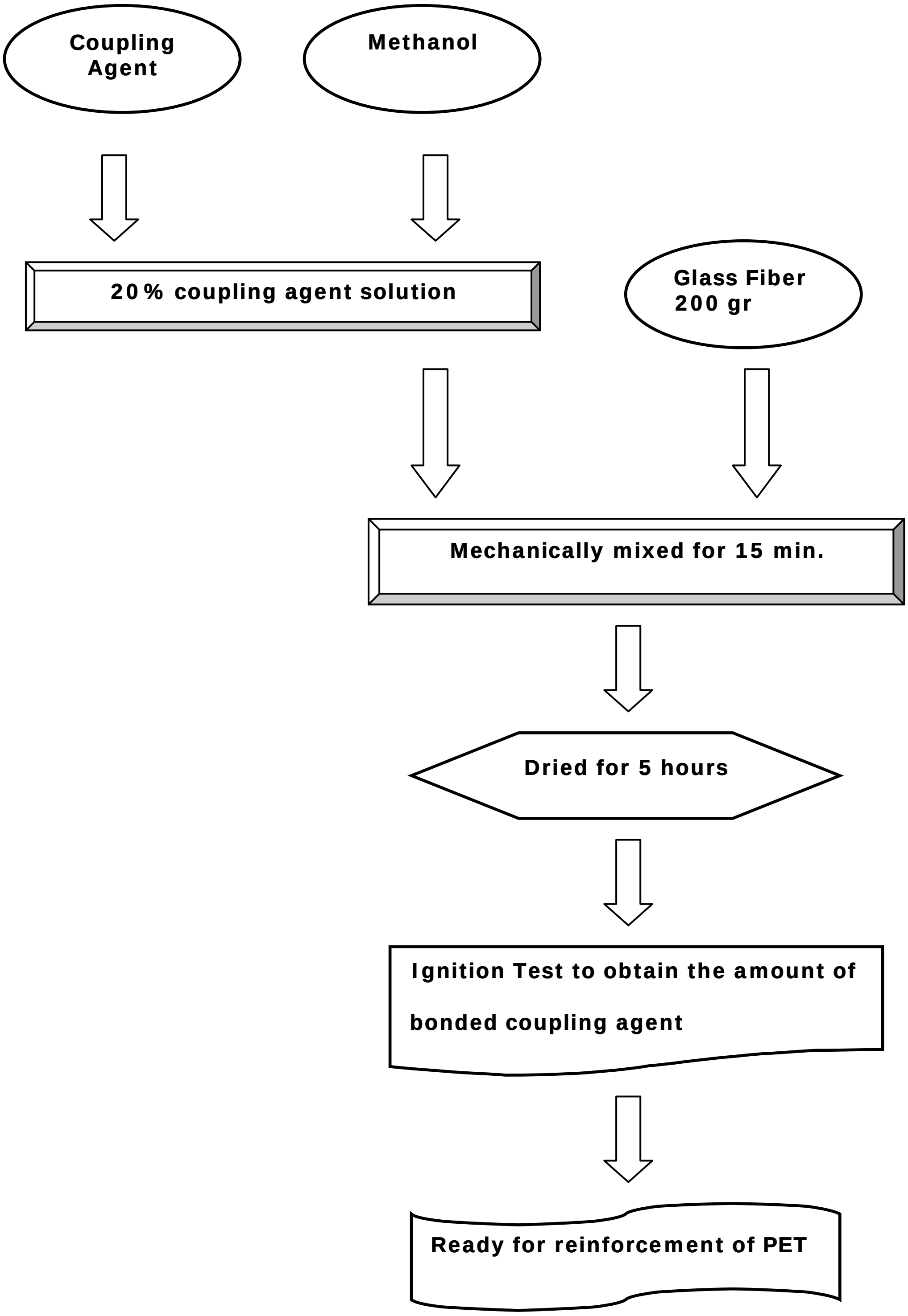


**Figure 3.6** Flowchart of the procedure for fiber treatment

## 3.3 Preparation of Glass Fiber/PET Composites

Before starting the processing experiments, PET and GF were dried at 160°C for 4 hours and at 120°C for 2 hours respectively. Glass fiber/PET composites were produced in two steps. Firstly, a corotating twin screw extruder (Thermo Prism TSE16TC) with a screw diameter of 16mm and L/D ratio of 24, was used to produce glass fiber/PET composites in pellet form. Three different sets were performed during experimental studies. In the first set, composites were produced using original glass fiber purchased from the manufacturer with different amounts of glass fiber content. PET was reinforced by 10, 15, 30, 45 and 55 weight % glass fiber with constant extrusion process parameters; screw speed of 230rpm and feed rate of 20g/min. The temperature profile in the extruder was 290-285-280-275-230°C. According to the results obtained from mechanical tests, a constant composition, 30 % GF/PET, was chosen for the rest of experiments. Different extrusion process parameters, such as, 170rpm and 290rpm screw speed at constant 20g/min feed rate, and 10g/min and 15g/min feed rate at constant screw speed of 230rpm were applied to observe the effects of processing parameters on final properties of composites. In the third set, glass fibers supplied by the manufacturer were treated with the four different coupling agents. After that, PET was reinforced with treated glass fibers at constant 30%GF/70%PET composition, 230rpm screw speed and 15g/min feed rate. These process parameters were selected according to results of mechanical tests. The same process temperature profile was used through the extrusion. After the completion of extrusion steps, produced pellets were prepared in sheet form (15cmx15cmx2mm) by compression molding technique to obtain the specimens for characterization experiments. Before starting the compression molding, the GF/PET composites in pellet form were dried at 120°C for 4 hours. Compression molding process parameters were kept constant at each set of experiment at molding temperature of 280°C, pressure of 150 bar, preheating time of 5 minutes and holding time of 8 minutes. As cooling method, quenching was applied in order to eliminate negative effects of crystallized PET. During slow cooling, structure of PET changes from amorphous to crystalline structure and crystalline structure shows more brittle property. Figure 3.7 and 3.8 illusrate twin screw extruder and compression molding machines, respectively. In addition, the procedure for preparation of GF/PET composites is shown in Figure 3.9.

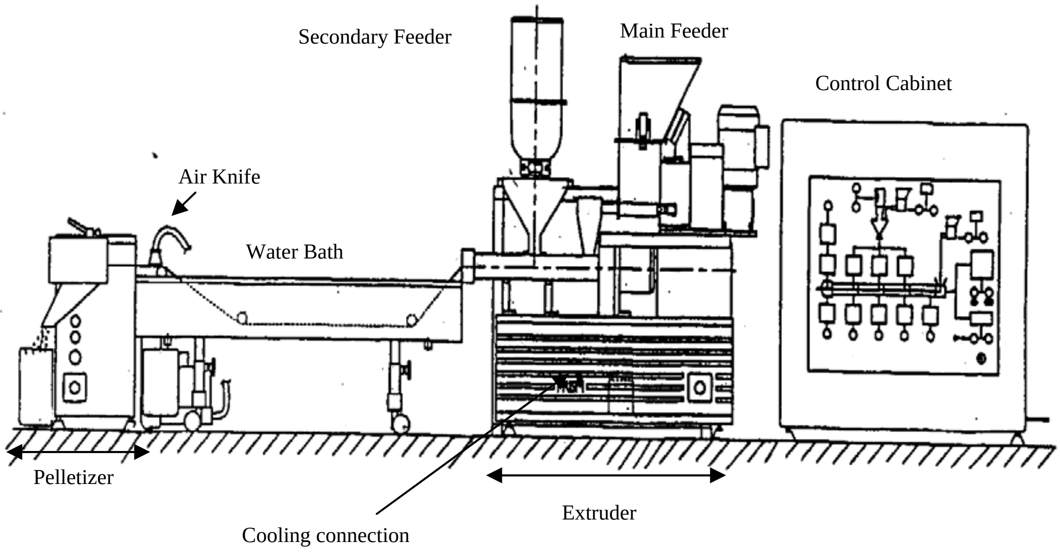


**Figure 3.7** Twin screw extruder

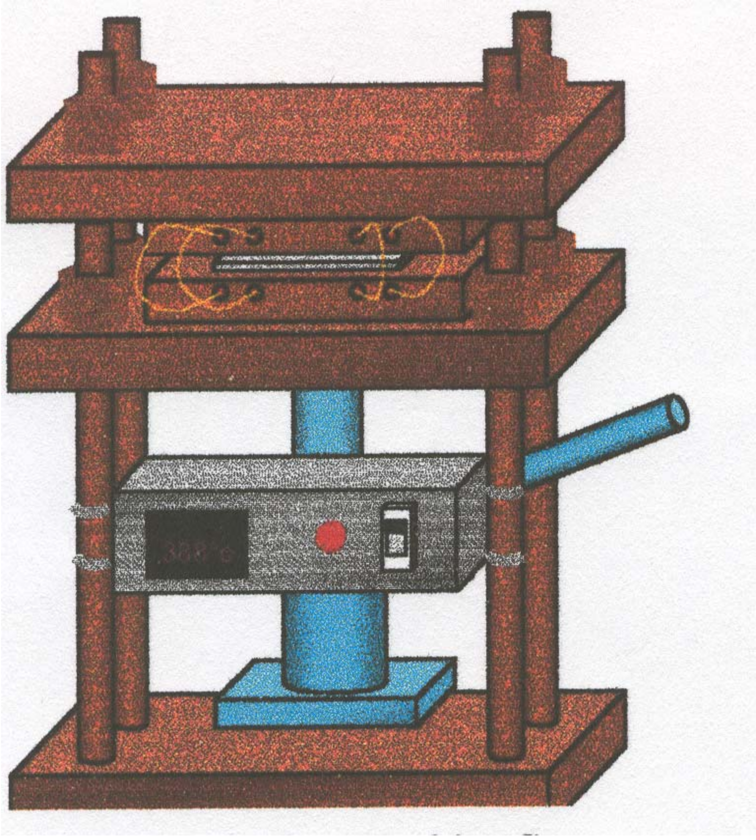


**Figure 3.8** Compression Molding Machine

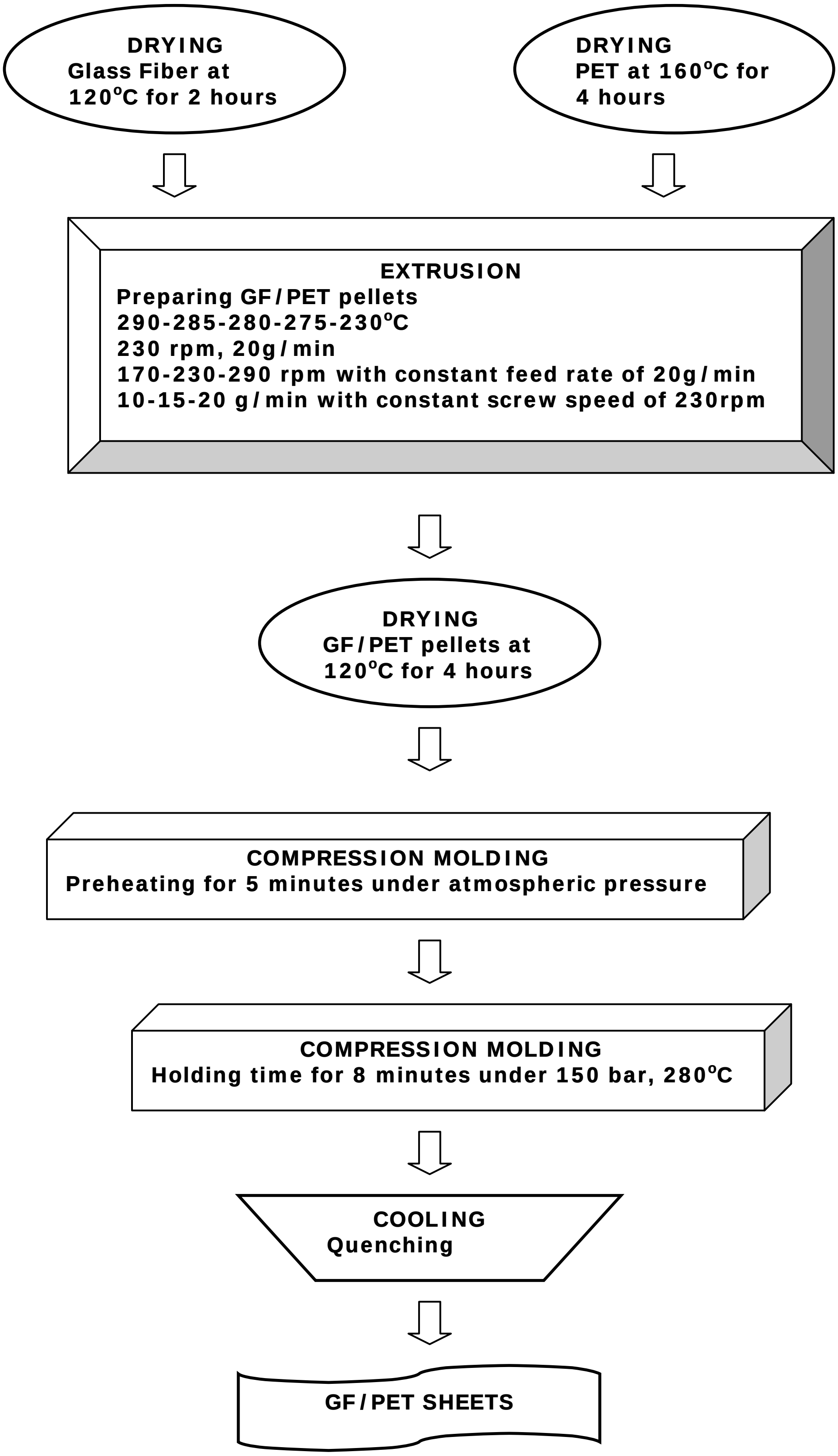


**Figure 3.9** Flowchart for preparation of GF/PET composites

### 3.4 Characterization Experiments

In order to observe the effects of glass fiber on final properties of the composites, samples were characterized in terms of morphological, thermal and mechanical properties. In addition to these, fiber length distribution was determined by using ignition tests to obtain information on change in fiber length before and after processing.

#### 3.4.1 Scanning Electron Microscopy (SEM) Analysis

The fractured surfaces of the samples from tensile tests were investigated by using a JEOL JSM-6400 Scanning Electron Microscope in order to observe glass fiber distribution in composite and interface interaction between fiber and polymer. The fractured surfaces were coated with a thin layer of gold. The SEM photographs were taken at different magnifications.

#### 3.4.2 Differential Scanning Calorimetry (DSC) Analysis

Differential Scanning Calorimetry analyses were performed by using a General V4.1C DuPont 2000. Analyses were carried out from 20$^{o}$C to 300$^{o}$C with 20$^{o}$C/min heating rate under nitrogen atmosphere and quenching method was followed during cooling. Because of the amorphous and crystalline behaviors of PET at different temperatures, two heating runs were performed in order to observe thermal effect on samples.

### 3.4.3 Tensile Tests

All tensile tests performed at room temperature. For each composite, average results of at least five measurements with standard deviations were reported and the error bars were drawn according to the standard deviations.

Tensile tests were performed by using a Lloyd 30K Universal Testing Machine according to ASTM D638-91a (Standard Test Method for Tensile Properties of Plastics) with dimensions specified in Type MII illustrated in Figure 3.10 and Table 3.7, respectively. The extension rate was 3mm/min. At least 5 specimens were tested for each set of experiments. Tensile strength, elongation at break and tensile modulus values were determined.

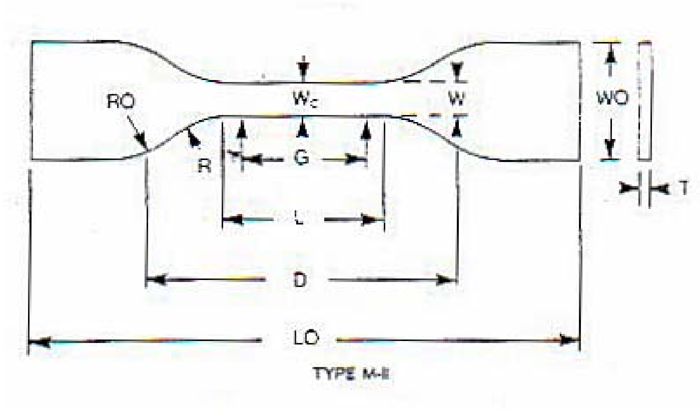


**Figure 3.10** Tensile test specimen

**Table 3.7** Dimensions of tensile test specimen

| dimensions | specimen dimensions, mm |
|---|---|
| W- width of narrow section | 6 |
| L- length of narrow section | 33 |
| W0- width of overall | 25 |
| L0- length of overall | 115 |
| G- gauge length | 25 |
| D- distance between grips | 80 |
| R- radius of fillet | 14 |
| R0- outer radius | 25 |
| T- thickness | 4 |

### 3.4.4 Ignition Tests

Ignition tests were performed according to ASTM D2584-68 (Standard Test Method for Ignition Loss of Cured Reinforced Resins) in order to determine the amount of glass fiber in the composite, to obtain the amount of bonded coupling agent to the glass fibers and to determine fiber length distribution and number average fiber length in the glass fiber/PET composite after processing.

#### 3.4.4.1 Coupling Agent Content Analysis

Glass fibers were treated by using four different types of coupling agents as explained in section 3.2. 5 grams of sample were put in a crucible separately for each type of treated glass fiber. At least five crucibles were prepared for each sample. All samples were ignited at a temperature of 565°C for a holding time of 3 hours in a furnace. Then, the ignited samples were cooled in a desicator and weighed in order to obtain the bonded amount of coupling agent. The bonded amount of coupling agent was decided to be 1% (weight%) of glass fiber which was used during teatment.

#### 3.4.4.2 Fiber Length Distribution Measurements

Approximately 2 grams of produced glass fiber/PET composites from each set of experiment were ignited at a temperature of 565°C for a holding time of 5 hours in a furnace. At least 3 crucibles for each types of GF/PET composite were used to obtain glass fiber ashes. After completion of the ignition step, obtained glass fibers were put on the glass lamel and a small amount of water dropped on the fibers. It was waited until complete evaporation of water. Then, the glass fibers on the lamel were analyzed in order to observe fiber length distribution by using an optical microscope which sends image to the screen. Also, fiber length was viewed and examined under the microscope. For each sample approximately 360 fibers were evaluated.

# CHAPTER IV

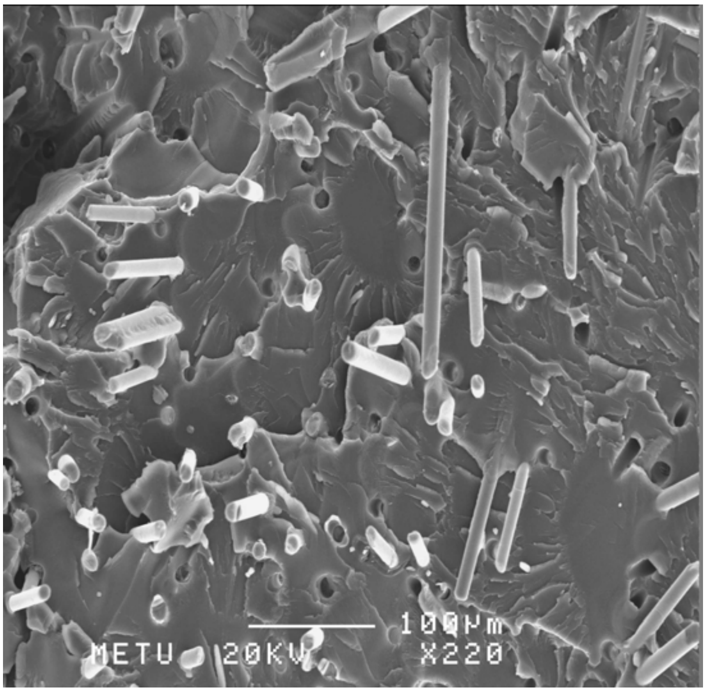
# RESULTS AND DISCUSSION

## 4.1 Effects of Glass Fiber Content on Morphological, Thermal and Mechanical Properties of GF/PET Composites

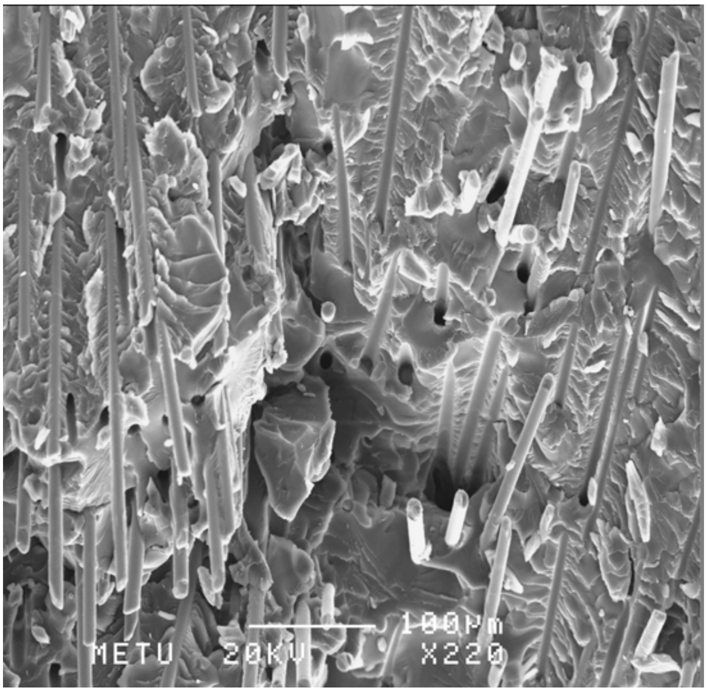
### 4.1.1 Scanning Electron Microscopy Analysis

In order to observe the morphologies of glass fiber/PET composites at different glass fiber content SEM analyses were performed. The SEM micrographs of GF/PET composites at 10%, 15%, 30%, 45% and 55% glass fiber contents are shown in Figures 4.1 through 4.3.

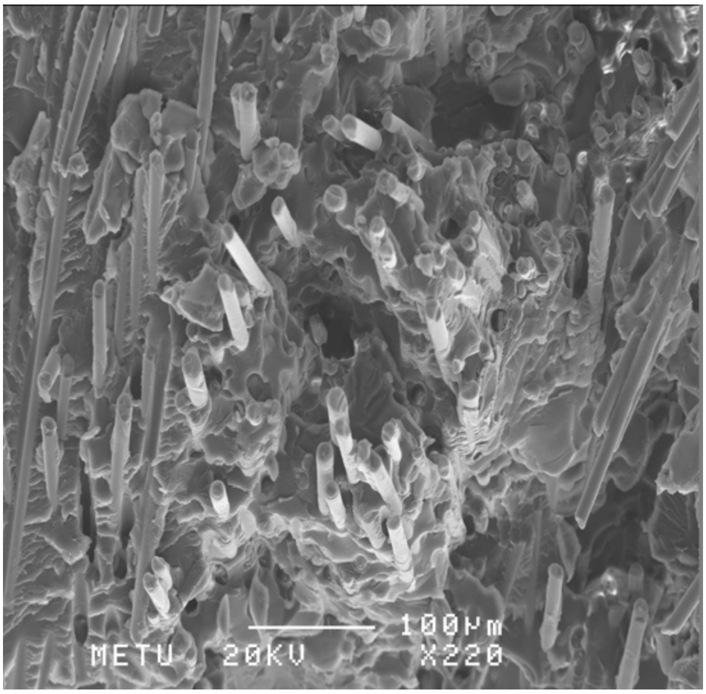
Figure 4.1 illustrates that as the glass fiber concentration in the GF/PET composites increases, interaction between the glass fiber and PET matrix increases. At low concentration such as 10% (Figure 4.1a) and 15% GF content (Figure 4.1b), uncracked and long fibers are observed and most of the fibers are pulled out from the matrix. Increasing glass fiber concentration results in an increase in the adhesion between fiber and polymer which improves mechanical properties of the composites. When the SEM micrographs of the composites with 30% and 45% GF (Figures 4.1c and 4.1d) is compared with those of 10% and 15% GF (Figures 4.1a and 4.1b), a well dispersion of glass fibers at higher GF contents can be observed without any significant orientation.



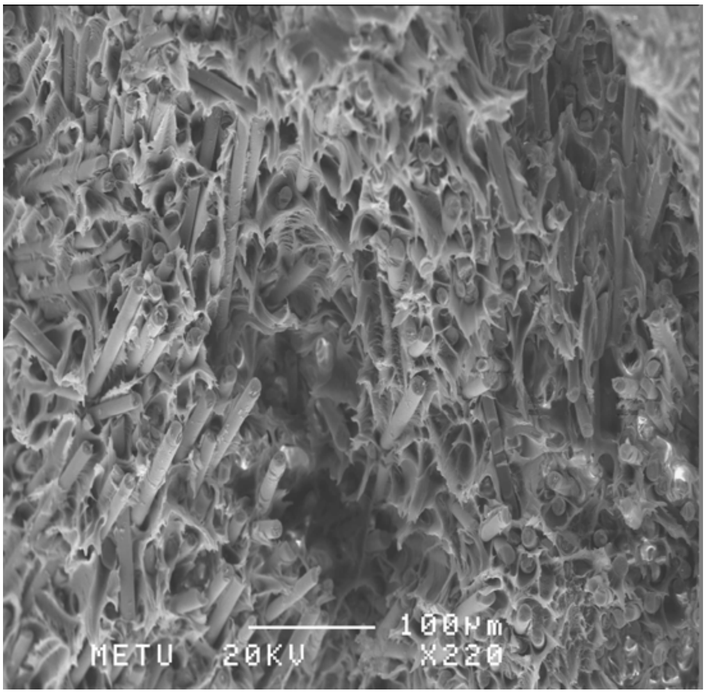
(a) 10 wt% GF / 90 wt% PET



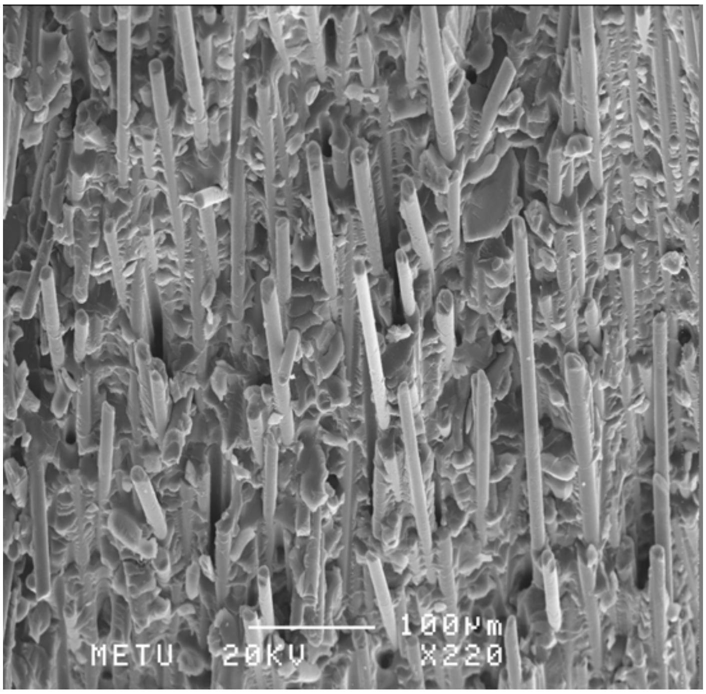
(b) 15 wt% GF / 85 wt% PET



(c) 30 wt% GF / 70 wt% PET



(d) 45 wt% GF / 55 wt% PET



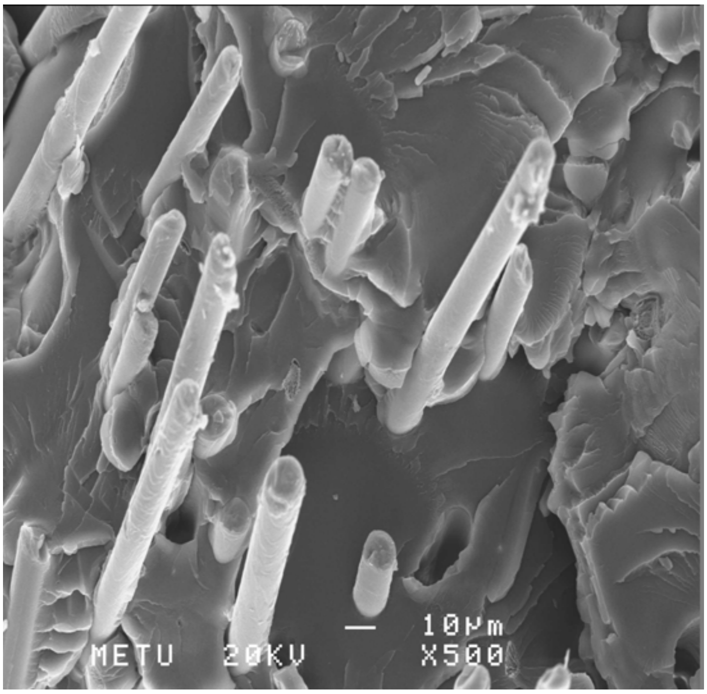
(e) 55 wt% GF / 45 wt% PET

**Figure 4.1** SEM micrographs of GF/PET composites containing a)10 wt% b) 15 wt% c) 30 wt% d) 45 wt% and e) 55 wt% GF (x220 magnification)

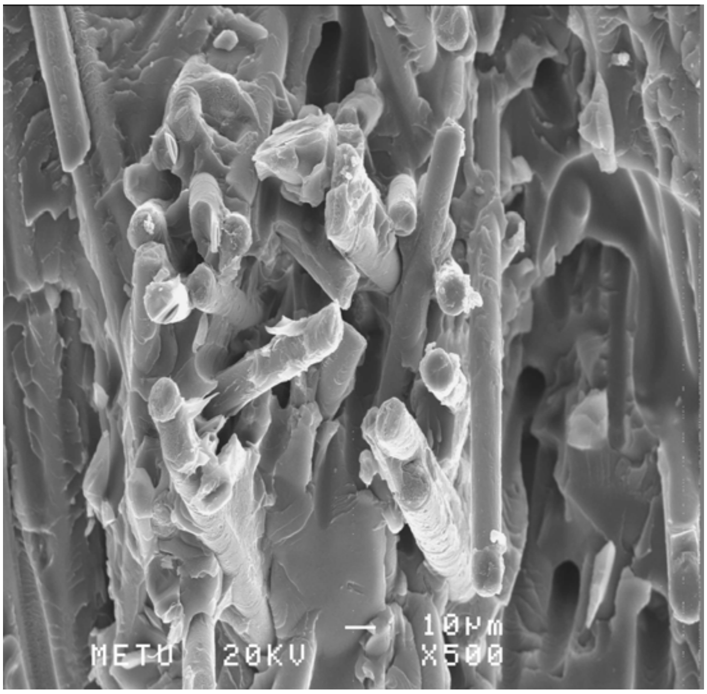
Figure 4.1e shows the morphology of the composite with excess amount of GF (55% GF / 45% PET). It is observed that the fibers are placed one on top of each other which reduces the interaction between the filler and the matrix. Therefore, a reduction in mechanical properties may be expected due to decreasing adhesion between the glass fiber and PET.

SEM micrographs of the composites containing 10% GF and 55% GF are presented in Figure 4.2 with x500 magnification. 10% GF/90% PET composite indicates the existence of low degree of adhesion. The photograph of 55% GF/45% PET show that there is poor orientation. For these composites, relatively low tensile properties with respect to other GF concentrations were obtained as can be seen in Section 4.1.3.

The glass fibers which were used in this part of the study were as received form, which were supplied by the manufacturer. A good and strong adhesion between the interfaces of the glass fiber and PET was observed (Figure 4.3a and 4.3b). Silane coupling agent which is 3-APE was responsible for the interaction between the fiber and matrix.

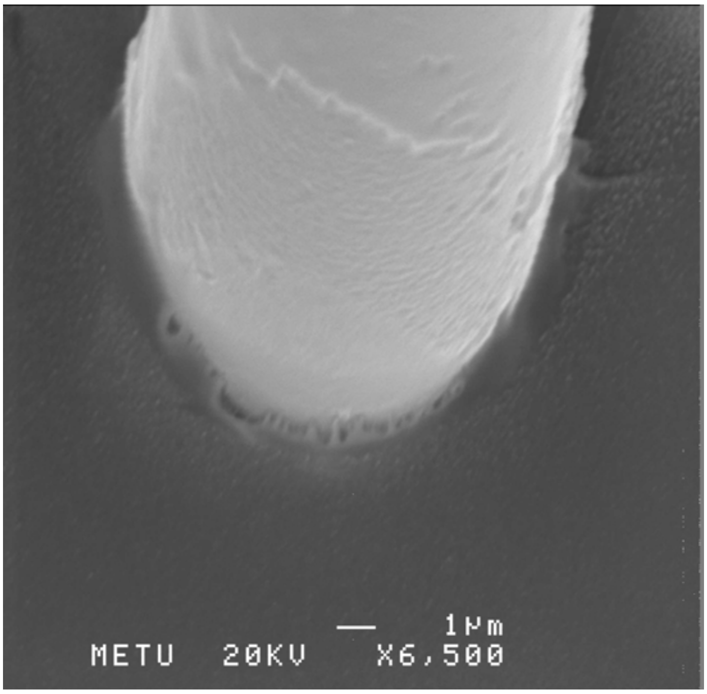


(a) 10 wt% GF / 90 wt% PET

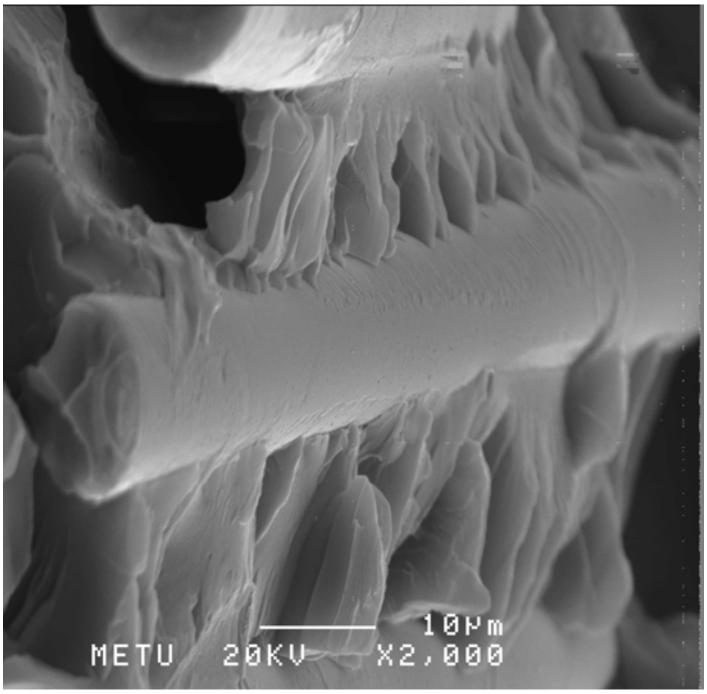


(b) 55 wt% GF / 45 wt% PET

**Figure 4.2** SEM micrographs of GF/PET composites containing a) 10% GF and b) 55% GF (x500 magnification)



(a) 10 wt% GF / 90 wt% PET



(b) 30 wt% GF / 70 wt% PET

**Figures 4.3** SEM micrographs of interfacial adhesion between glass fiber and PET a) 10% GF/90% PET (x6500 magnification) b) 30% GF/70% PET (x2000 magnification)

### 4.1.2 Differential Scanning Calorimetry Analysis

Glass transition temperature ($T_g$), melting temperature ($T_m$) and heat of melting ($\Delta H_m$) of pure recycled PET and GF/PET composites are given in Table 4.1. As glass fiber concentration increases, thermal properties of the composites do not change significantly when compared to the pure recycled PET.

A considerable increase in the degree of crystallinity of the composite with 30% GF, increases the stiffness and strength, and leads to the dimensional stability of material.

**Table 4.1** DSC results for GF/PET composites with different amounts of glass fiber

| **Material** | $T_{g,\ PET}$ ( $^{o}$C ) | $T_{m,\ PET}$ ( $^{o}$C ) | $\Delta H_{m,\ PET}$ (J / gr PET) | **% Crystallinity** |
|---|---|---|---|---|
| **PURE RPET** | 81.15 | 254.51 | 23.23 | 16.8 |
| **%10 GF/PET** | 77.74 | 254.13 | 20.71 | 15.0 |
| **%15 GF/PET** | 78.85 | 254.42 | 19.01 | 14.8 |
| **%30 GF/PET** | 81.26 | 255.33 | 33.61 | 24.4 |
| **%45 GF/PET** | 79.91 | 253.48 | 22.45 | 16.3 |
| **%55 GF/PET** | 78.12 | 254.12 | 27.29 | 19.8 |

* $\Delta H_m^{o}$ for pure PET ; 138 J/g [19]

### 4.1.3 Tensile Tests

The stress-strain curves for representative samples illustrated in Figure 4.4. All the corresponding data of this figure are given in Table A1.1. The tensile strength, Young's Modulus and % Elongation (tensile strain at break) values of the composites with respect to glass fiber content are shown in Figures 4.5 through 4.7. All the data in the figures are given in Table A.1.2, A.1.3 and A.1.4.

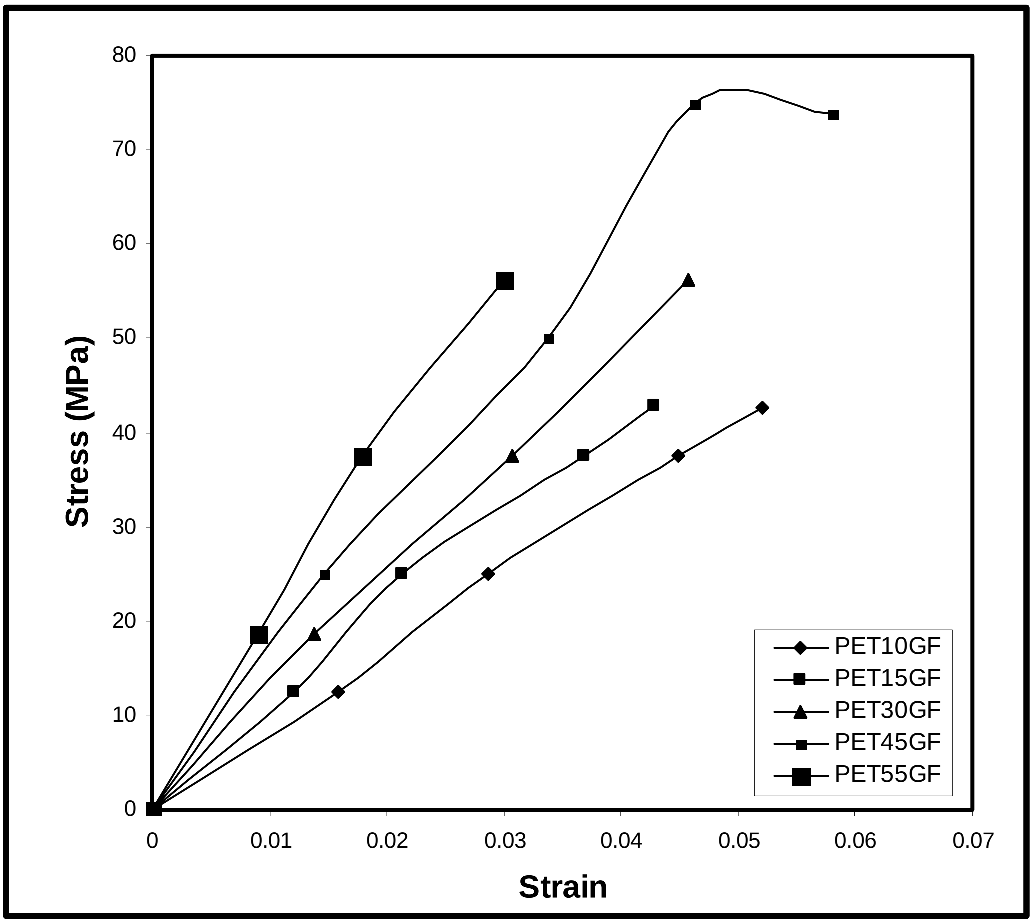


**Figure 4.4** Stress-Strain curve of GF/PET composites with different glass fiber contents

#### 4.1.3.1 Tensile Strength

Figure 4.5 represents the tensile strength of GF/PET composites with respect to glass fiber content. The average values of the results and standard deviations are given in Table A.1.2. As can be seen from the figure, tensile strength increases with increasing amount of glass fiber. A high content of reinforcement material makes the polymer stronger. Therefore an improvement in the mechanical behavior of the composite is obtained. As the glass fiber concentration increases, fiber-polymer interaction also increases and then composites have high tensile strength values. However, in the usage of excess amount of glass fiber, such as in the case of 55%GF/45%PET composites, reinforcement properties of glass fibers reduce as a result of low interaction between the fiber and the polymer. Because, glass fibers place locally in the matrix or they place one on the top of the other without interacting with the polymer. As seen in the figure, tensile strength values exhibit a maximum at 45%GF/55%PET composition. High tensile strength is not enough alone to decide on the best composition of GF/PET composite for the further experiments, since one of the objectives of this study is to improve the overall mechanical behaviour of the polymer by using relatively low amount of reinforcement material.

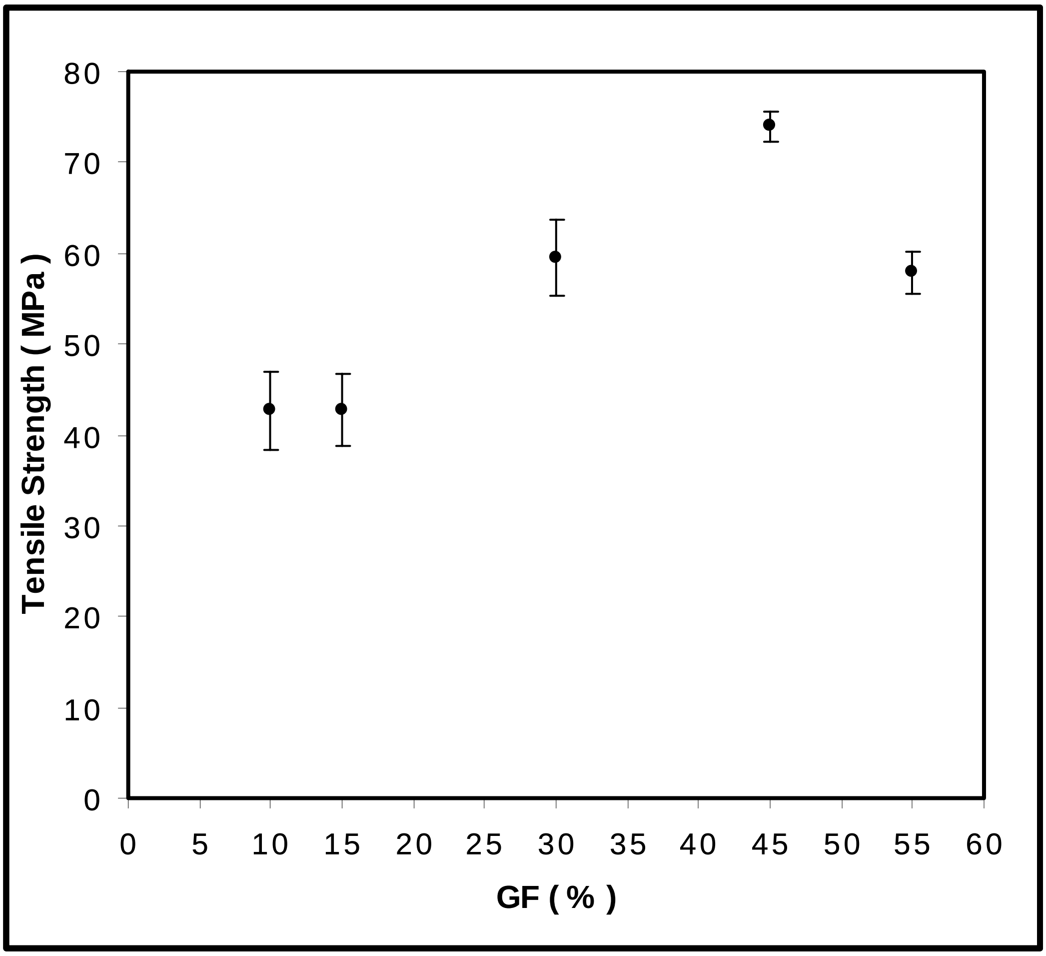


**Figure 4.5** Tensile Strength (MPa) versus GF content (%)

#### 4.1.3.2 Tensile (Young's) Modulus

Tensile moduli of the composites increase with increasing amount of glass fiber as shown in Figure 4.6. Table A.1.2 shows the data represented in this figure. It is expected that incorporation of glass fiber having high modulus to the matrix results in an increase in the stiffness of the composite. Other than that, as the glass fiber content increases, the interaction between glass fiber and PET increases and this enables composites having high moduli. At the maximum glass fiber content of 55% tensile modulus begins to decrease due to the higher fiber/fiber interaction.

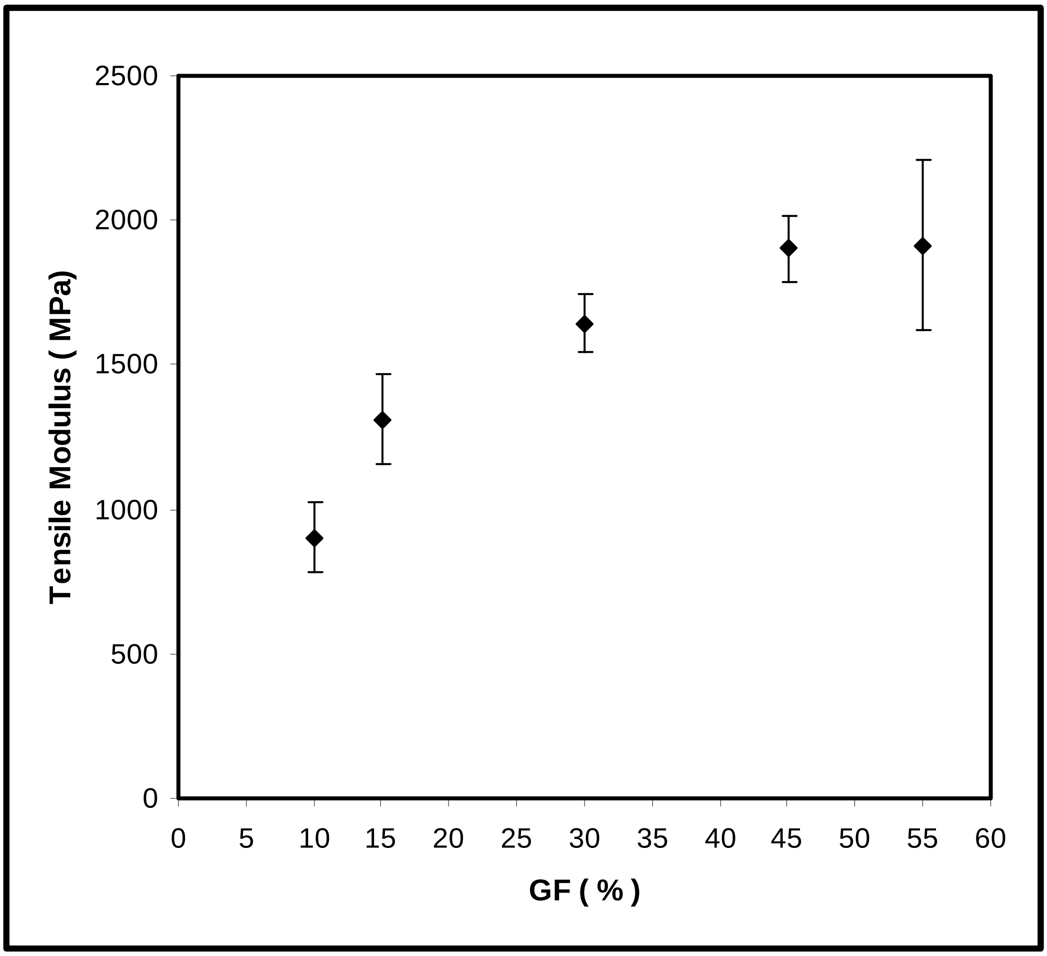


**Figure 4.6** Tensile Modulus (MPa) versus GF content (%)

### 4.1.3.3 Strain at Break (% Elongation)

Figure 4.7 shows the % elongation values with respect to glass fiber content (see Table A.1.4 for corresponding data). As the glass fiber content increases, strain at break values do not show a consistent increasing or decreasing trend, rather it fluctuates. At 15% and 55% glass fiber content, there exist low % elongation values of the composites with respect to the other concentrations of the GF. This is somewhat unexpected for 15% GF, but expected for 55% GF since glass fiber is a rigid material and high concentrations of GF, imparts brittle behavior to the composites.

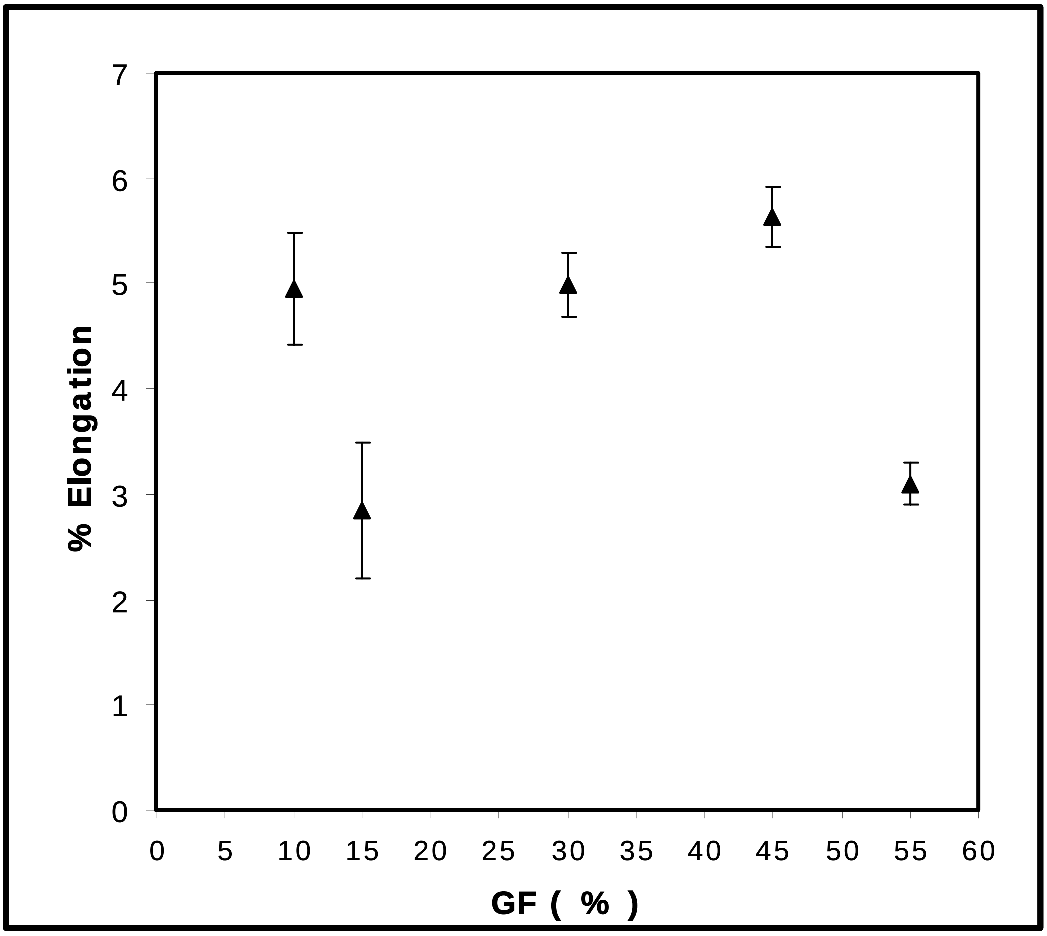


**Figure 4.7** % Elongation versus GF content (%)

### 4.1.4 Ignition Tests

#### 4.1.4.1 Glass Fiber Content

Table 4.2 shows the results of glass fiber content obtained by ignition tests after processing the materials and the original composition of GF/PET composite which is adjusted through calibration in the extrusion. Glass fiber concentrations in the GF/PET composites from ignition tests are approximately 5% more than the original ones which are planned. Although the sensitive calibration of feeding of the materials at the beginning of the extrusion is applied, the slippery and electrostatic properties of glass fibers cause the fibers to move together which results in some local increase of glass fiber content during processing.

**Table 4.2** Glass fiber content in the GF/PET composites

| Planned GF Content (%) | Obtained GF Content (%) |
|---|---|
| 10 | 13.90 |
| 15 | 20.37 |
| 30 | 35.97 |
| 45 | 47.20 |
| 55 | 60.98 |

#### 4.1.4.2 Fiber Length Distribution

Number average fiber length and fiber length distributions with respect to glass fiber content are shown in Figures 4.8 and 4.9. The corresponding data are given in Table A.2. A decrease of number average fiber length is obtained from 10% up to 30% GF and then an increase from 30% GF to 55% GF content is observed. This is the result of interaction between the fibers and polymer. As seen in SEM micrographs (Figures 4.1 through 4.3) the interfacial adhesion was poor at the lower concentrations of glass fiber. This results in uncracked and pulled out fibers, however at the glass fiber concentrations of 30% and 45%, interfacial adhesion between fiber and polymer is higher, which reduces the fiber length. Other than that, higher fiber/fiber interaction causes the damage of the glass fibers.

The fiber length is not effective alone on the mechanical behaviour of composites. Even though having long fibers gives high tensile strength and modulus, the effects of the interaction between fiber and polymer and volume fraction of the glass fibers compete with each other and therefore an increase or decrease in mechanical properties can be obtained. Figure 4.9 shows that the fiber length distribution denses around fiber length of 300 μm. The highest frequency in the range of the average fiber length is observed for the composite containing 30% glass fiber.

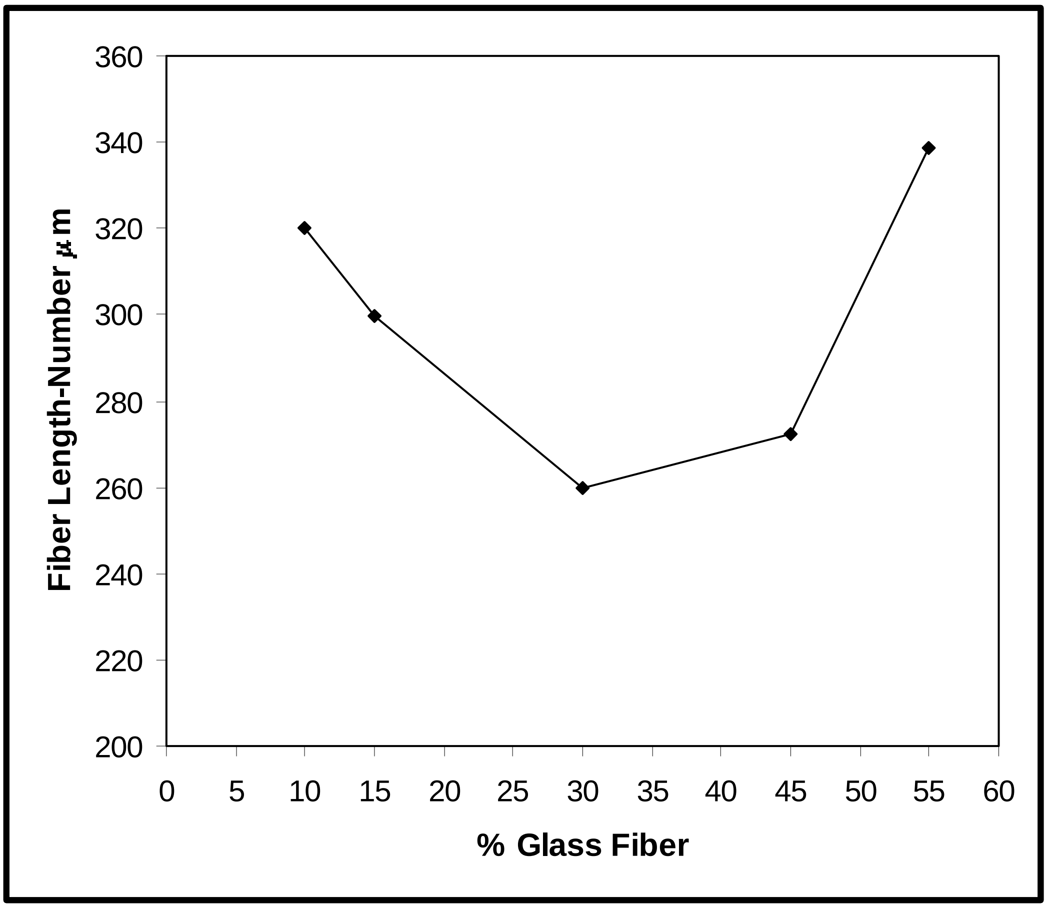


**Figure 4.8** Number average fiber length ($L_n$) versus GF content(%)

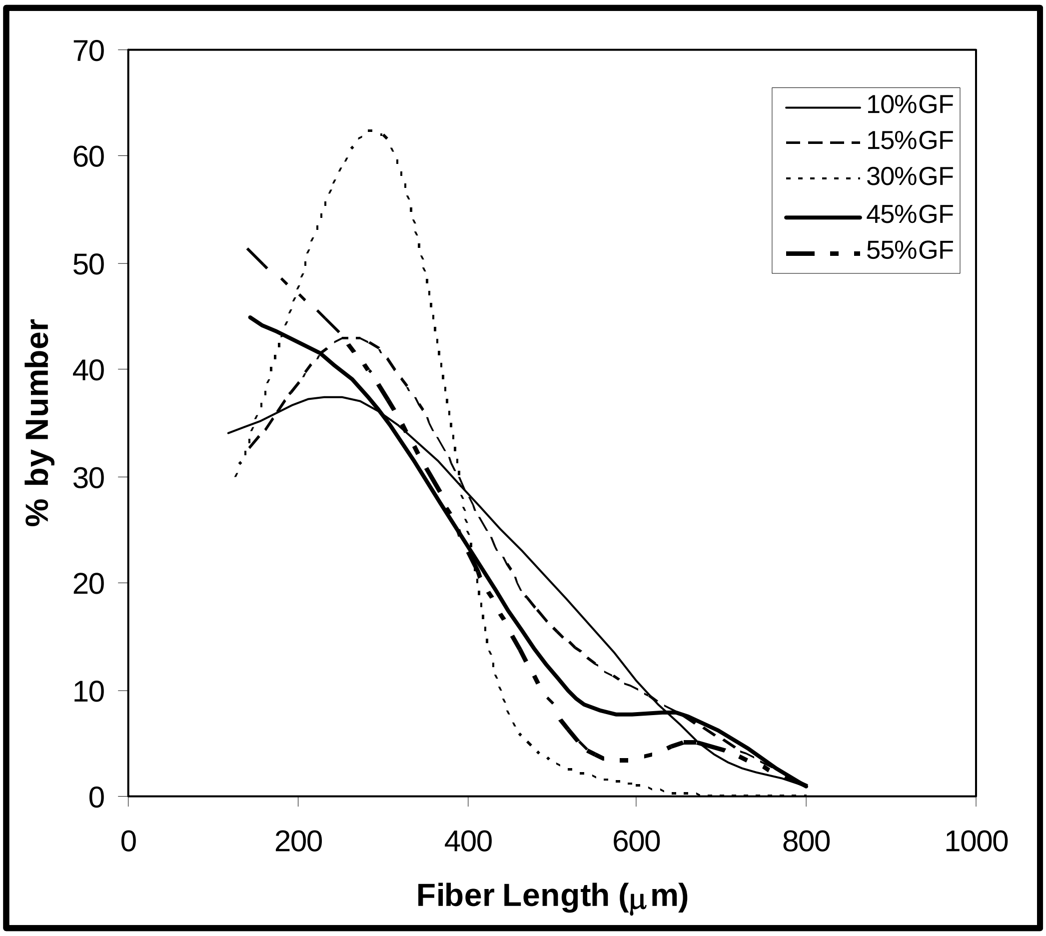


**Figure 4.9** Fiber length distribution at various GF content

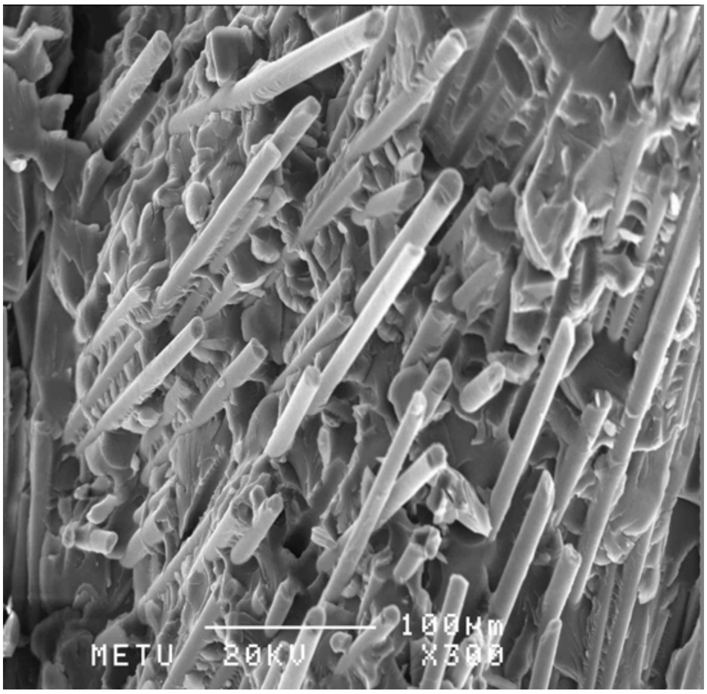
## 4.2 Effects of Process Parameters on Morphological, Thermal and Mechanical Properties of GF/PET Composites

In order to observe the effects of process parameters such as screw speed and feed rate on the morphological, thermal and mechanical behaviour of GF/PET composites, a constant composition of 30%GF/70%PET composite was chosen.

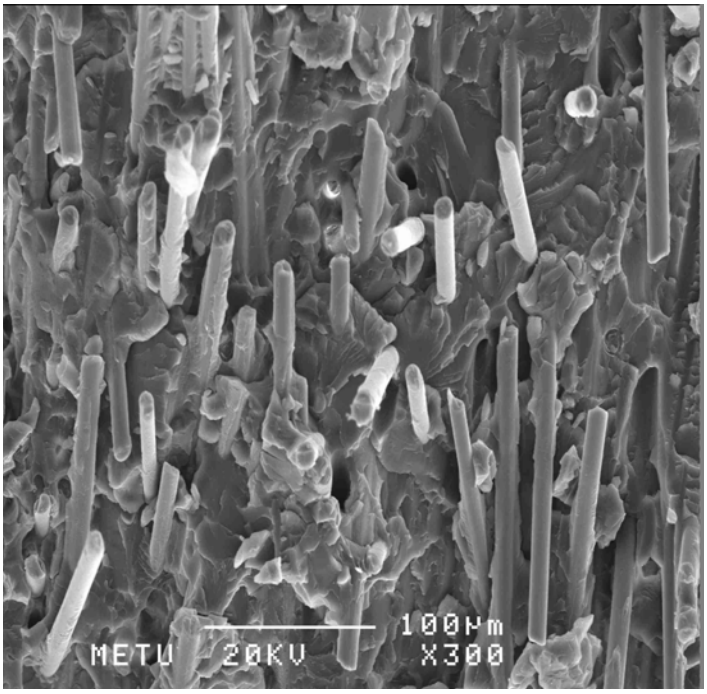
### 4.2.1 Scanning Electron Microscopy Analysis

The effect of screw speed (170, 230 and 290 rpm) at constant feed rate (20 g/min) on the morphologies of GF/PET composites are shown in Figures 4.10.a and b, and 4.11. It can be said that there is a slight decrease in fiber length with increasing screw speed from 170 rpm to 290 rpm. High screw speed gives more shearing, which causes a decrease in fiber length.

Figures 4.12 and 4.13 show the SEM photographs of the composites processed at 10, 15 and 20 g/min feed rate and 230 rpm screw speed. As can be seen from the figures fiber allingment is reduced with increasing feed rate, which results in lower tensile properties.



(a) Screw speed of 170 rpm



(b) Screw speed of 290 rpm

**Figure 4.10** SEM micrographs of GF/PET composites processed at feed rate of 20 g/min and different screw speeds a) 170 rpm and b) 290 rpm (x300 magnitude)

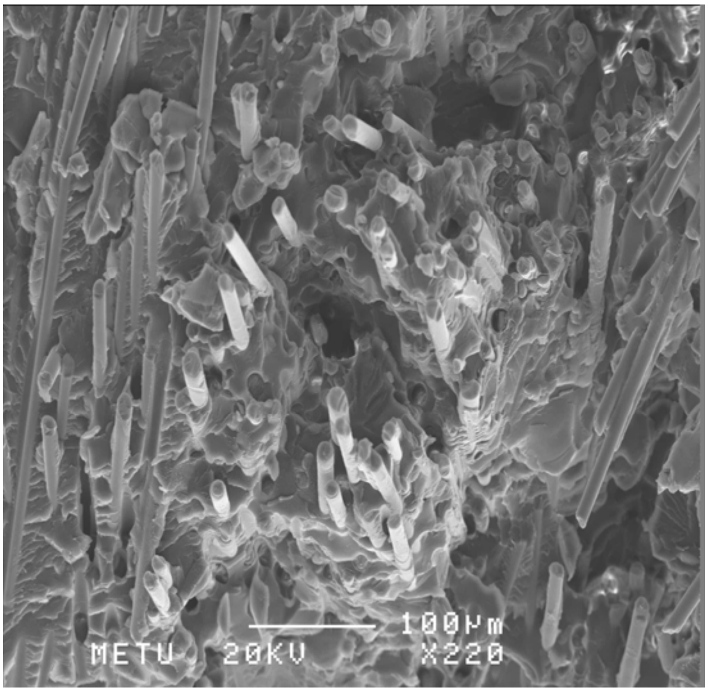
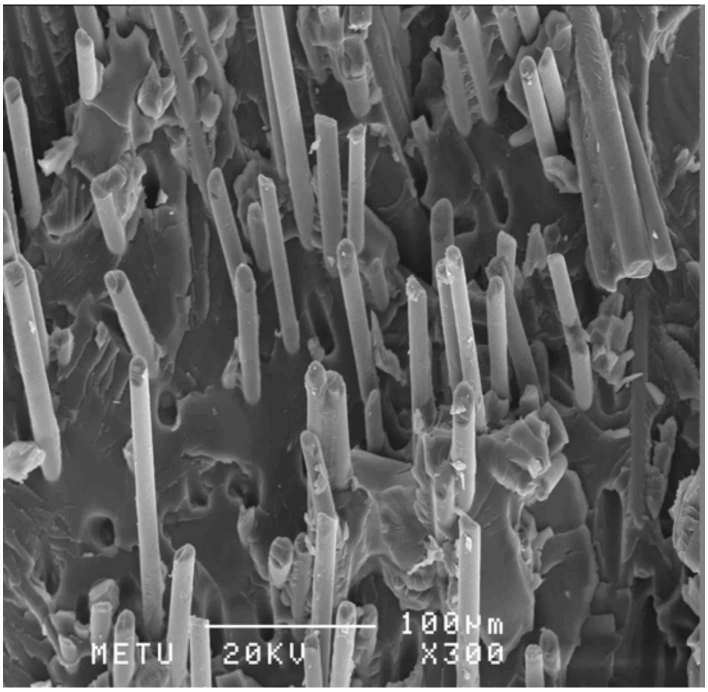
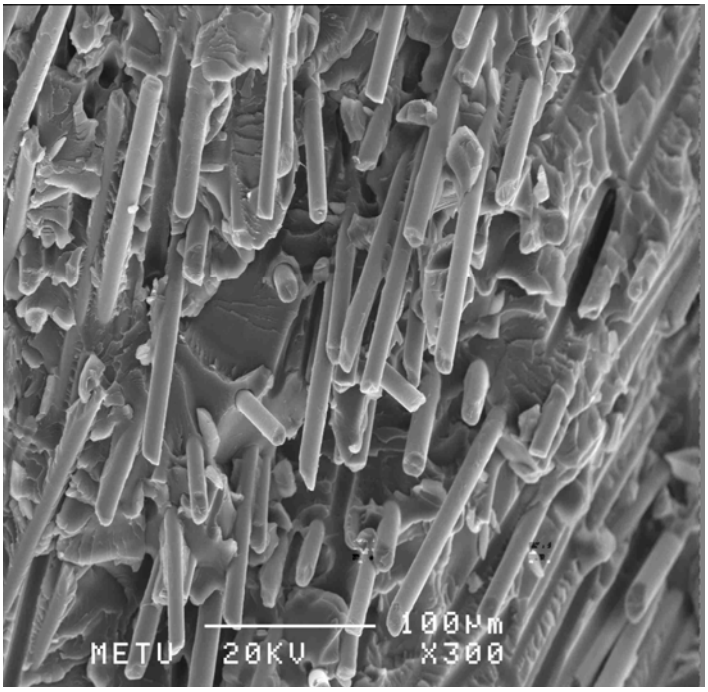


**Figure 4.11** SEM micrograph of GF/PET composite processed at feed rate of 20 g/min and screw speed of 230 rpm (x220 magnitude)



(a) Feed rate of 10 g/min



(b) Feed rate of 15 g/min

**Figure 4.12** SEM micrographs of GF/PET composites processed at screw speed of 230 rpm and different feed rates of a) 10 g/min b) 15 g/min (x300 magnitude)

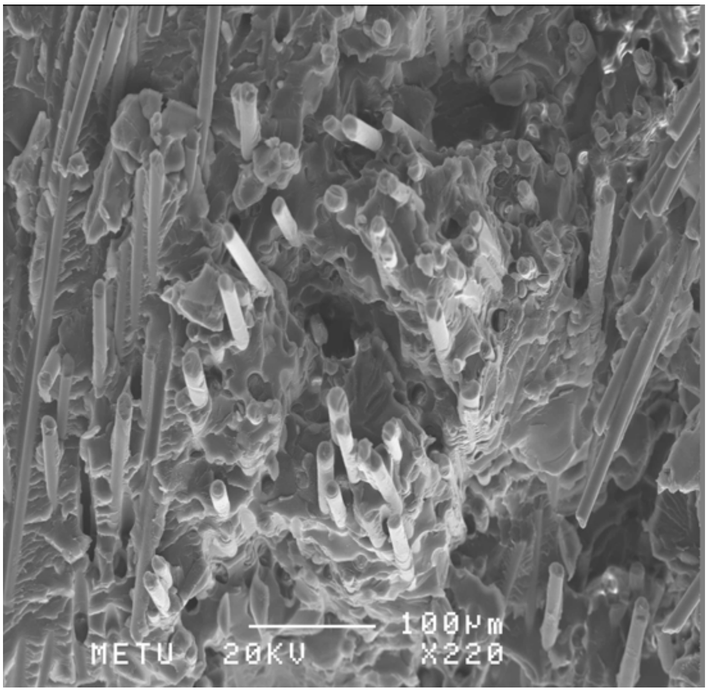


**Figure 4.13** SEM micrograph of GF/PET composite processed at screw speed of 230 rpm and feed rate of 20 g/min (x220 magnitude)

### 4.2.2 Differential Scanning Calorimetry Analysis

The results of DSC analysis with respect to screw speed at constant feed rate and with respect to feed rate at constant screw speed are shown in Table 4.3 and 4.4 respectively. Glass transition temperature shows a maximum at 230 rpm. As screw speed increases, percent crystallinity values fluctuates and gives a lower degree of crystallization at 230rpm. At lower feed rates (10 and 15 g/min), glass transition temperature is lower than that of composite processed at feed rate of 20 g/min. % crystallinity values of the composites produced at low feed rates are somewhat higher than the one at 20 g/min. A maximum in degree of crystallinity is obtained at 15 g/min feed rate.

**Table 4.3** DSC results for GF/PET composites at different screw speeds

| **Material** | **$T_g$, PET ($^o$C)** | **$T_m$, PET ($^o$C)** | **$\Delta H_m$, PET (J / gr PET)** | **% Crystallinity** |
|---|---|---|---|---|
| **PURE RPET** | 81.15 | 254.51 | 23.23 | 16.8 |
| **%30GF/PET, 170rpm-20gr/min** | 75.70 | 253.10 | 45.26 | 32.8 |
| **%30GF/PET, 230rpm-20gr/min** | 81.26 | 255.33 | 33.60 | 24.4 |
| **%30GF/PET, 290rpm-20gr/min** | 75.34 | 252.70 | 71.01 | 51.5 |

* $\Delta H_m^o$ for pure PET ; 138 J/g [19]

**Table 4.4** DSC results for GF/PET composite at different feed rates

| Material | $T_g$, PET (°C) | $T_m$, PET (°C) | $\Delta H_m$, PET (J / gr PET) | % Crystallinity |
|---|---|---|---|---|
| **PURE RPET** | 81.15 | 254.51 | 23.23 | 16.8 |
| **%30GF/PET, 230rpm-10gr/min** | 75.11 | 254.12 | 39.77 | 41.0 |
| **%30GF/PET, 230rpm-15gr/min** | 76.11 | 253.23 | 68.73 | 49.8 |
| **%30GF/PET, 230rpm-20gr/min** | 81.26 | 255.33 | 33.60 | 24.3 |

* $\Delta H_m^o$ for pure PET ; 138 J/g [19]

### 4.2.3 Tensile Tests

The represantative stress-strain curves for the composites produced at different screw speeds (170, 230 and 290 rpm) and feed rate (10, 15 and 20 g/min) are illustrated in Figures 4.14 and 4.15. The data in the figures are given in Table A.1.1. The tensile strength, Young’s modulus and tensile strain at break (% elongation) values with respect to screw speed and feed rate are shown in Figures 4.16 through 4.21. The corresponding data in these figures are given in Table A.1.2, A.1.3 and A.1.4.

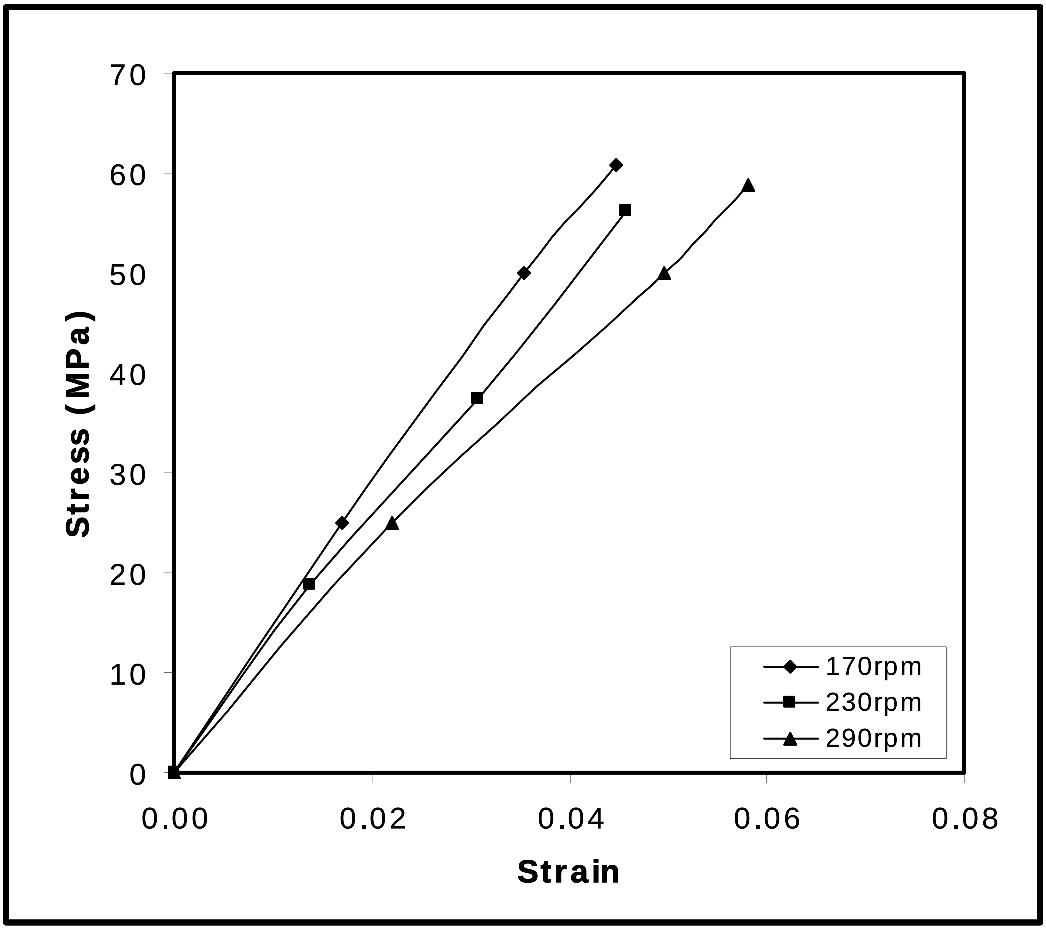


**Figure 4.14** Stress-Strain curves for composites processed at screw speeds of 170, 230 and 290 rpm

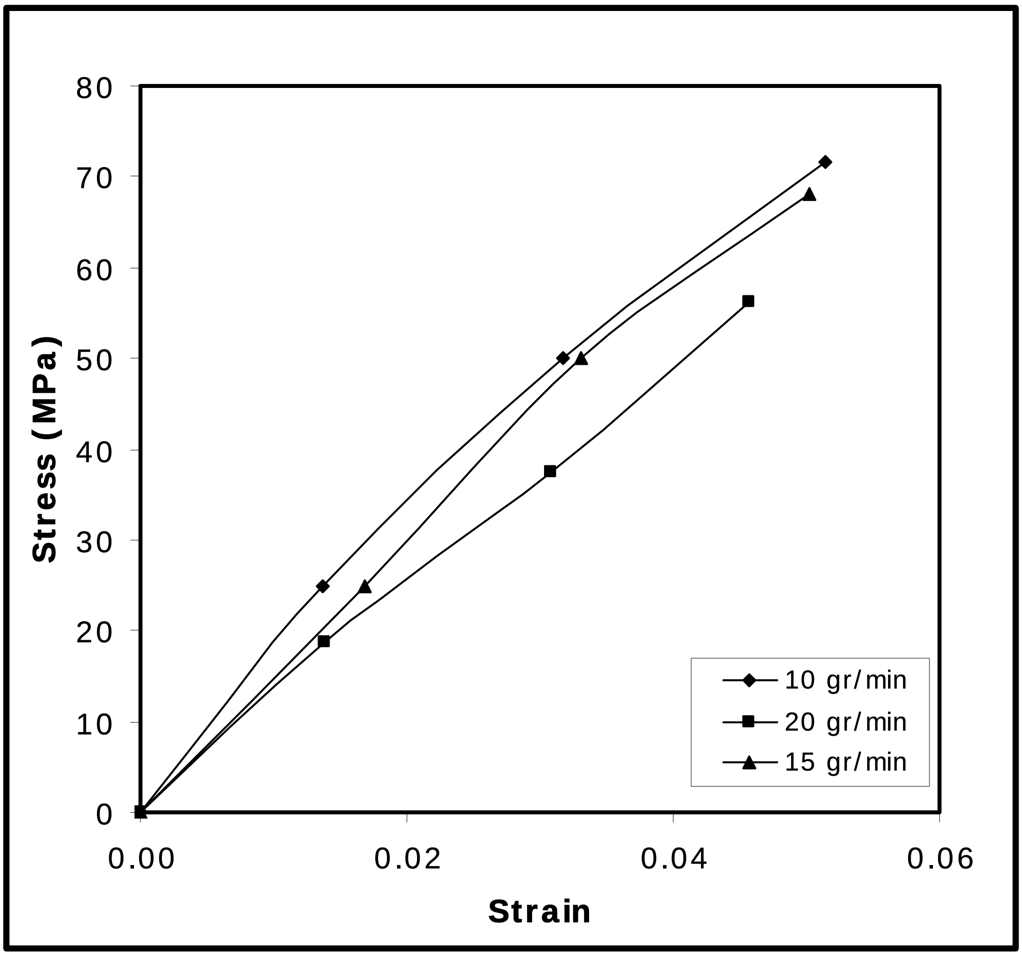


**Figure 4.15** Stress-Strain curves for the composites processed at feed rates of 10, 15 and 20 g/min

#### 4.2.3.1 Tensile Strength

The tensile strength values of GF/PET composites at increasing screw speed values of 170, 230 and 290 rpm are presented at Figure 4.16. It is observed that there is not any significant change in tensile strength with respect to increasing screw speed.

PET has a low viscosity at the temperatures above its melting point which is $253^0$C. This provides well mixing of glass fiber and polymer matrix during processing. When screw speed increases, it is expected that the fiber length decreases as a result of increasing shear rate. Therefore tensile strength of glass fiber reinforced composites decreases. Since the PET covers the glass fibers easily owing to its low viscosity, it does not allow a decrease in the fiber length.

When the feed rate is increased from 10 to 20g/min, the shear rate applied by the screws increases and number average fiber length decreases. This results in a decrease in tensile strength (Figure 4.17).

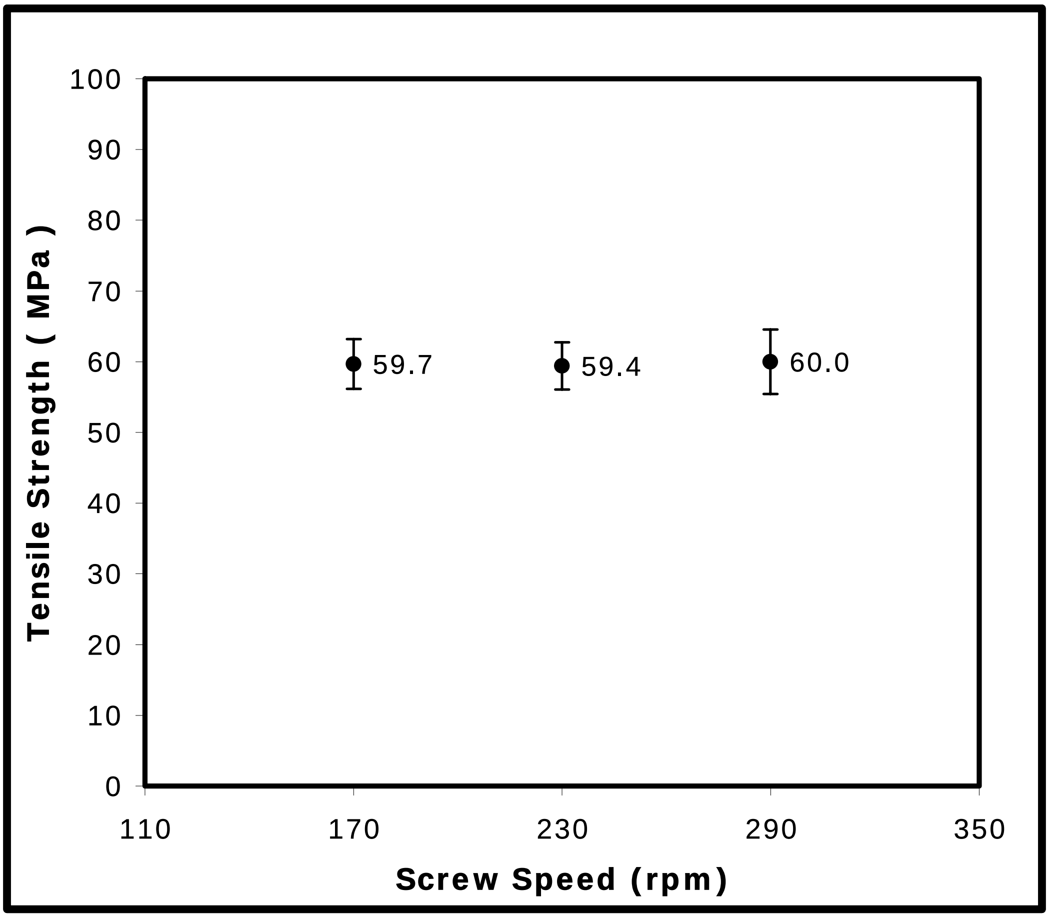


**Figure 4.16** Tensile Strength (MPa) versus screw speed (rpm) of GF/PET composites

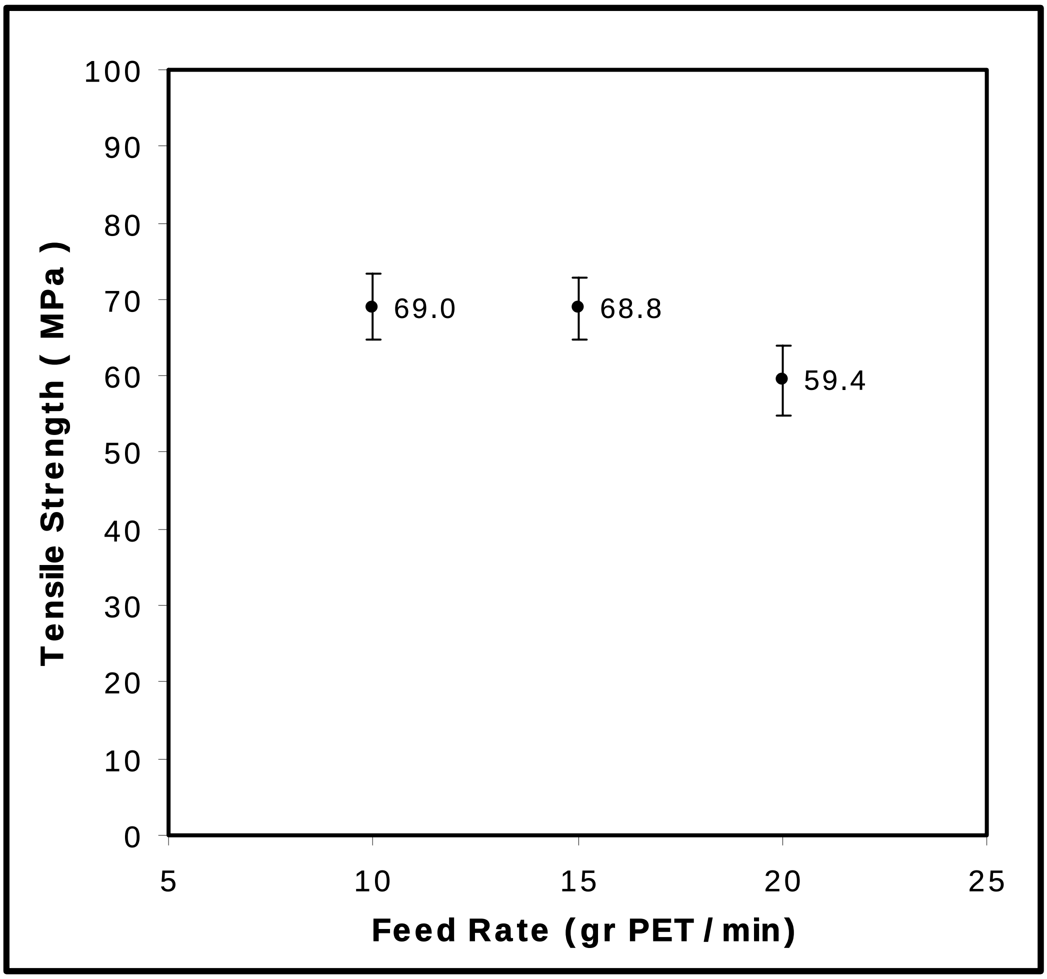


**Figure 4.17** Tensile Strength (MPa) versus feed rate (g/min) of GF/PET composites

#### 4.2.3.2 Tensile (Young's) Modulus

Figure 4.18 shows that as screw speed increases, tensile modulus of the composites decreases. Increasing screw speed implies high shearing which causes the decrease in fiber length and eventually the lower tensile modulus values.

Figure 4.19 illustrates the results of tensile modulus of GF/PET composites with respect to feed rate. Feed rate of 15 g/min gives a maximum in tensile modulus value. This can be due to somehow less effect of shearing in the process.

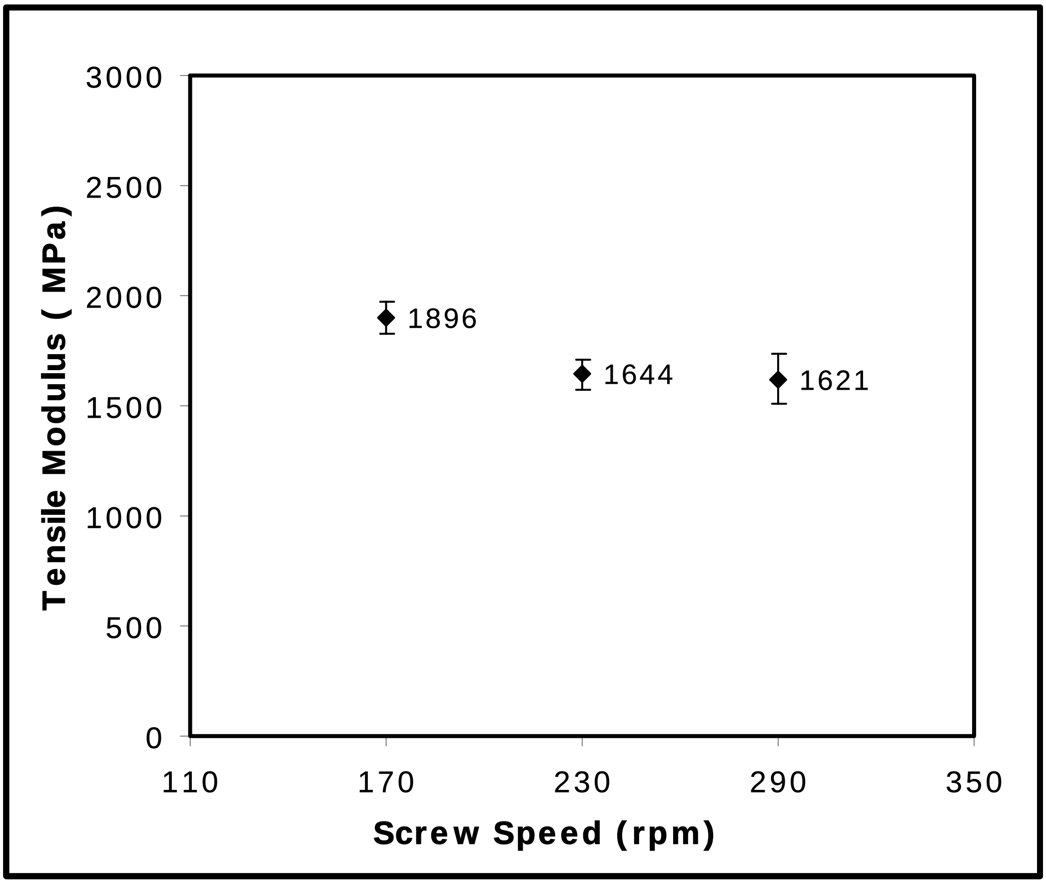


**Figure 4.18** Tensile Modulus (MPa) versus screw speed (rpm) of GF/PET composites

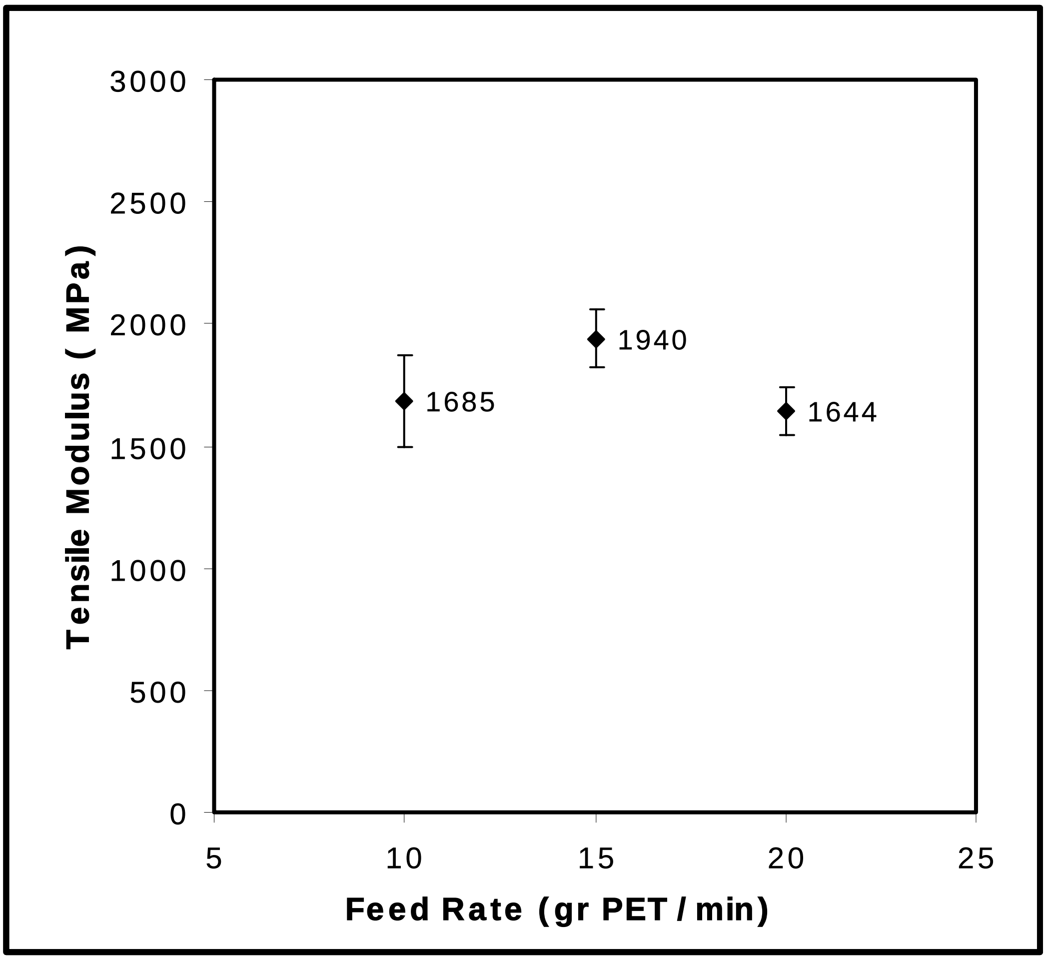


**Figure 4.19** Tensile Modulus (MPa) versus feed rate (g/min) of GF/PET composites

#### 4.2.3.3 Strain at Break (% Elongation)

The change in strain at break values with respect to screw speed and feed rate are shown in Figure 4.20 and 4.21 respectively. Increasing screw speed decreases fiber length which results in an increase in % elongation. Strain at break values can be confirmed with the fiber length distribution analyses given in part 4.2.4.2. Screw speed of 230 rpm gives the lowest number average fiber length which results in a maximum in % elongation. Since the composites at the screw speeds of 170 and 290 rpm have much higher number average fiber length, % elongation values of the composites become lower.

Figure 4.21 shows that there is somehow increase in strain at break values with feed rate, even though the number average fiber length decreases. This may be due to the high amount of the fibers per unit time with increasing feed rate.

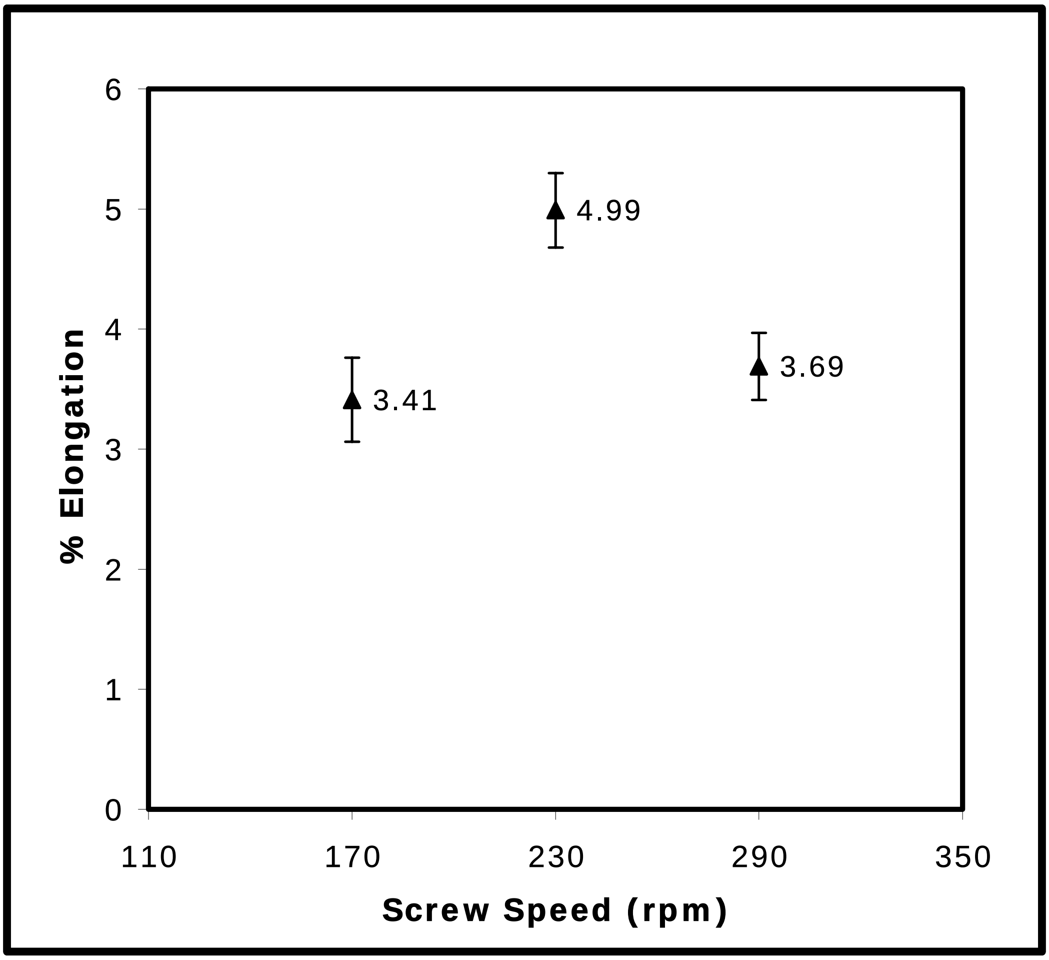


**Figure 4.20** % Elongation versus screw speed (rpm) for GF/PET composites

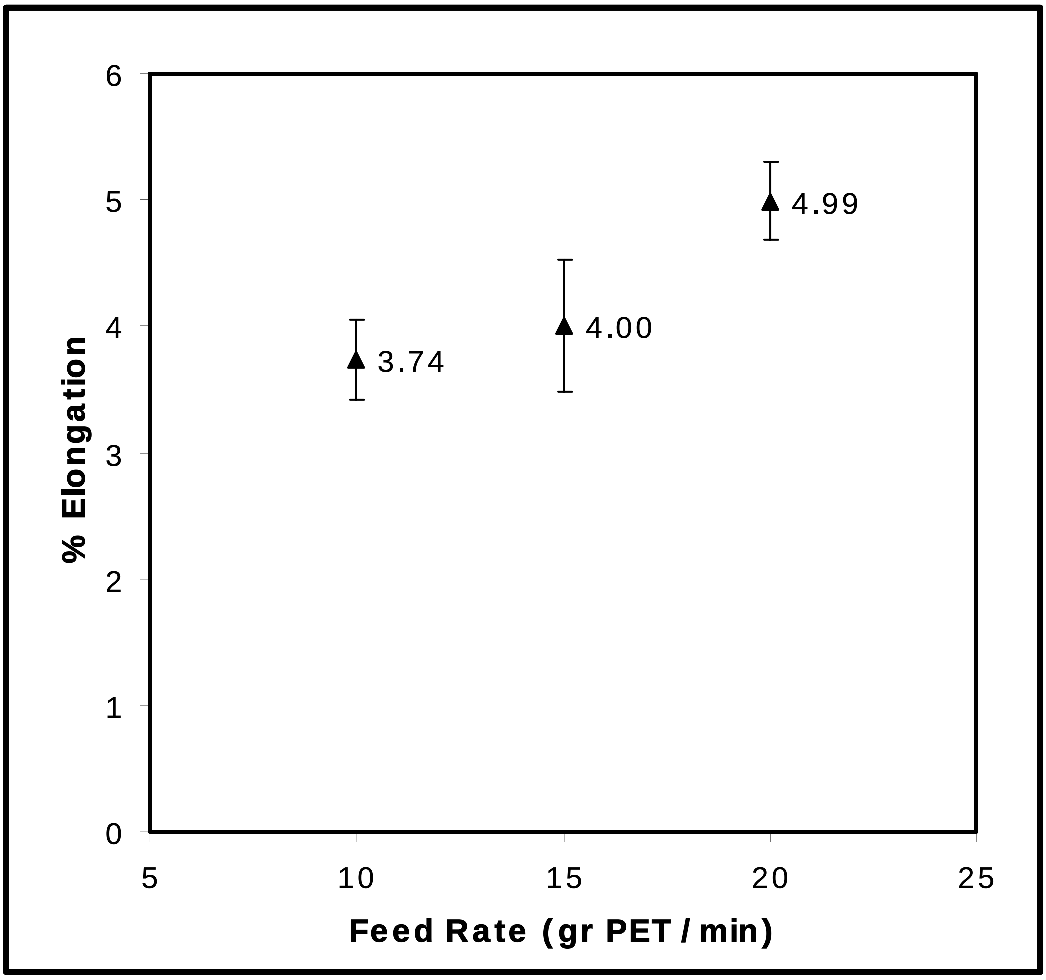


**Figure 4.21** % Elongation versus feed rate (g/min) for GF/PET composites

### 4.2.4 Ignition Tests

#### 4.2.4.1 Glass Fiber Content

Table 4.5 and 4.6 show the results of glass fiber content in the composites obtained from ignition tests and the original glass fiber concentration planned before extrusion. The values are given with respect to various screw speeds at constant feed rate and various feed rates at constant screw speed. Glass fiber concentrations of the composites obtained from ignition tests are approximately 6-7% more than the original ones that are planned due to the slippery characteristics of the fibers which causes glass fibers to accumulate locally during extrusion and results in an increase in fiber concentration.

**Table 4.5** Glass fiber content in the GF/PET composites produced at screw speeds of 170, 230 and 290 rpm and at feed rate of 20 g/min

| Planned GF Content ; | Obtained GF Content |
|---|---|
| 30% (170 rpm, 20g/min) | 36.70% |
| 30% (230 rpm, 20g/min) | 35.97% |
| 30% (290 rpm, 20g/min) | 35.80% |

**Table 4.6** Glass fiber content in the GF/PET composites produced at feed rates of (10,15 and 20 g/min) and at screw speed of 230rpm

| Planned GF Content ; | Obtained GF Content |
|---|---|
| 30% (10g/min, 230rpm) | 30.20% |
| 30% (15g/min, 230 rpm) | 36.20% |
| 30% (20g/min, 230rpm) | 35.97% |

### 4.2.4.2 Fiber Length Distribution

Number average fiber length and fiber length distributions with respect to screw speed and feed rate are shown in Figures 4.22 through 4.25. Data in the figures are given in Table A.2.

It is seen from Figure 4.22 that when the screw speed increases from 170 to 230rpm, fiber length decreases, however, when it is increased from 230 to 290rpm an increase in the fiber length is observed. This can be explained in terms of shear stress applied by the screws. At 170 rpm, screw speed is low but residence time for the fibers is high, and at 290 rpm this time screw speed is high but residence time is low. Therefore it is possible to obtain higher fiber lengths. But at 230 rpm, a minimum value for average fiber length is obtained due to high shearing effects in the extrusion.

Decrease in fiber length with increasing feed rate (Figure 4.24) can be explained as a result of the relation between the feed rate and the fill ratio which varies between 0 and 1. The fill ratio reaches one which can be related with the increase in the shear rate at high feed rates.

Figures 4.23 and 4.25 show that the fiber length distribution observed around fiber length of 300μm.

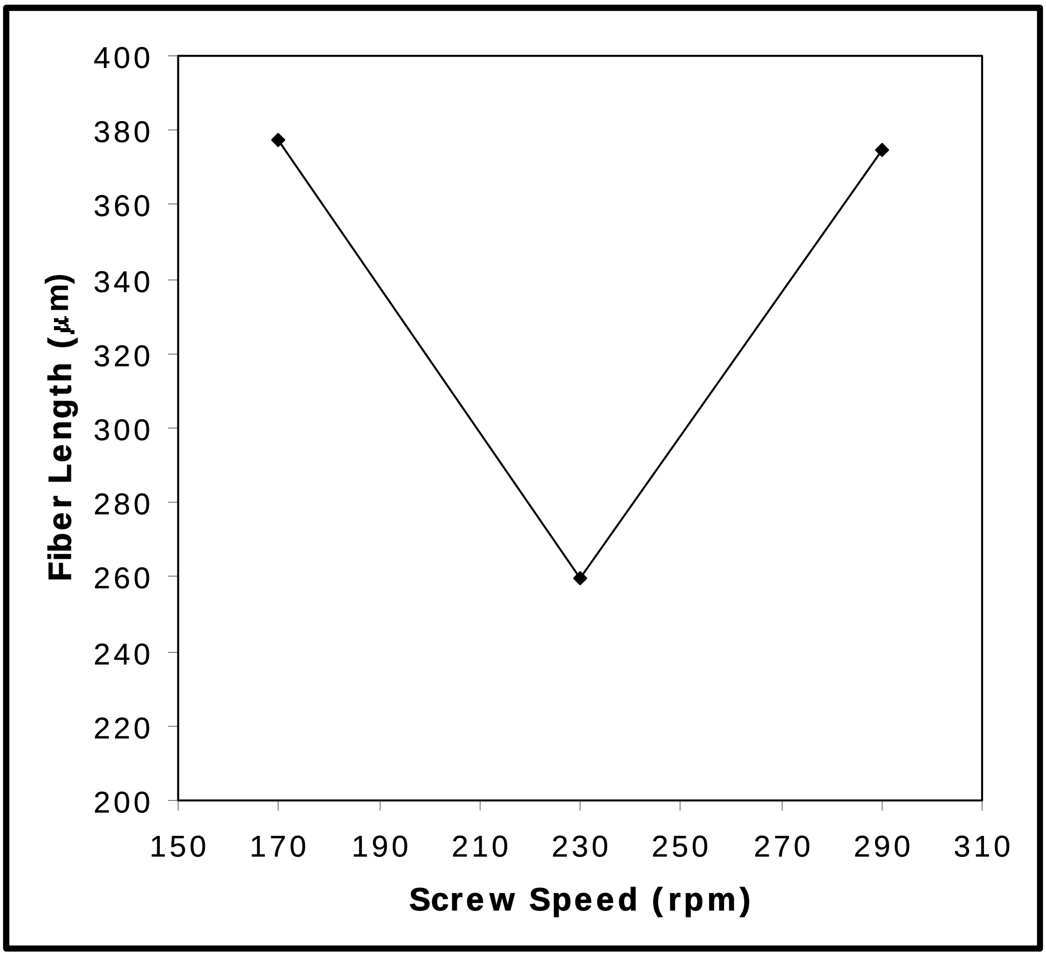


**Figure 4.22** Number average fiber length ($L_n$) versus screw speed (rpm) for GF/PET composites

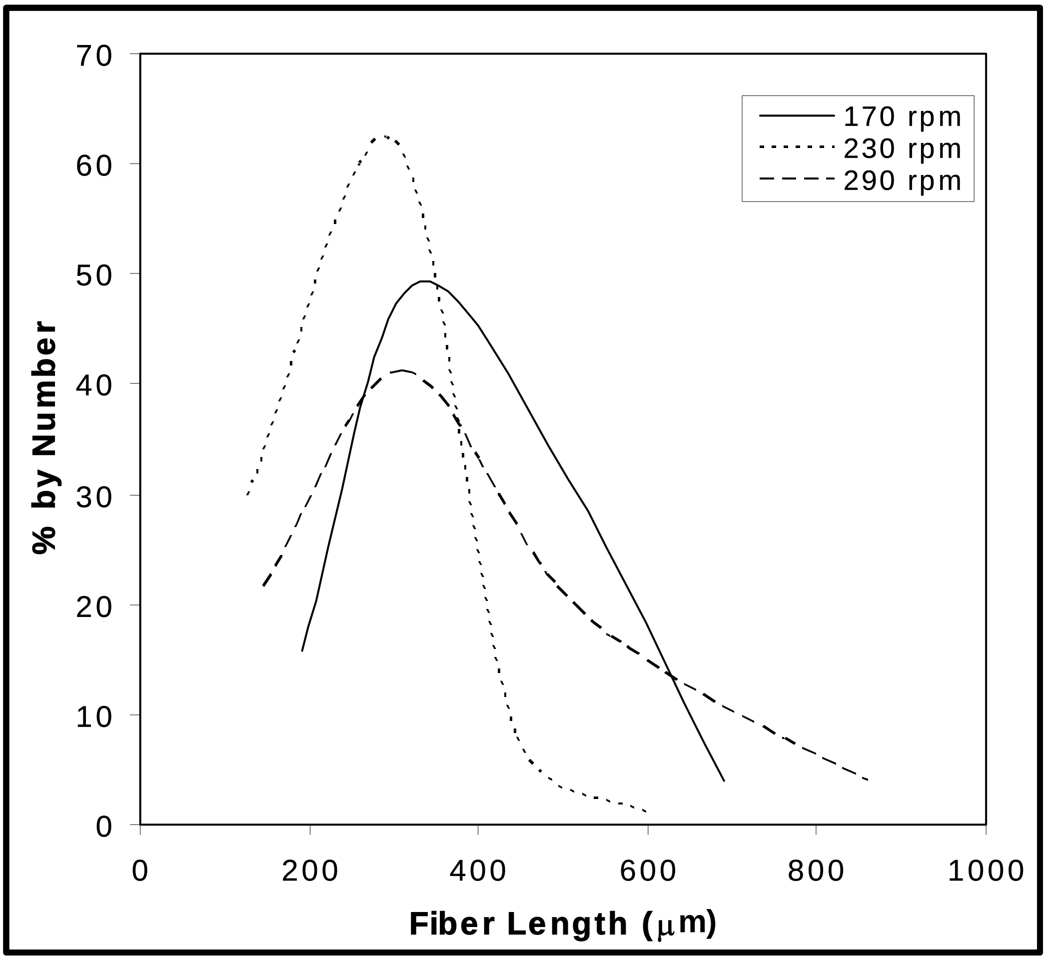


**Figure 4.23** Fiber length distribution of the GF/PET composites processed at various screw speeds (rpm)

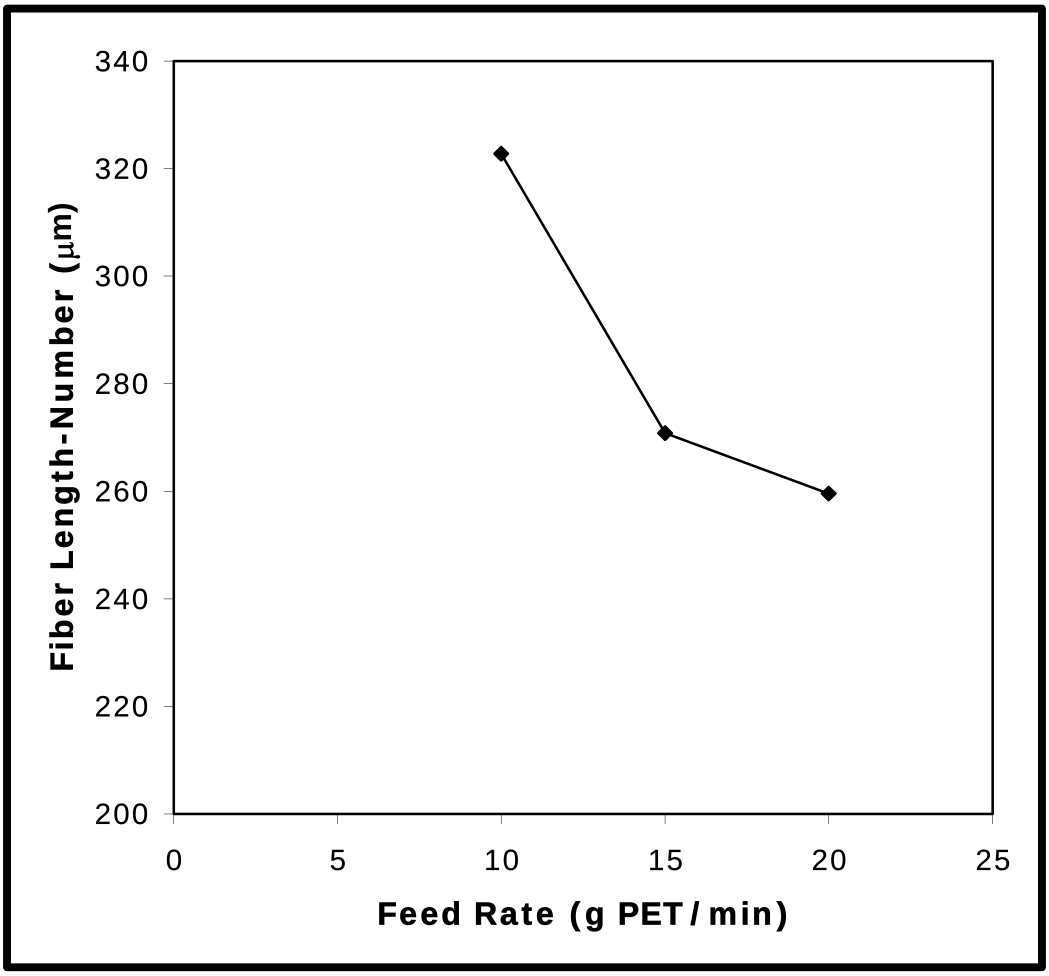


**Figure 4.24** Number average fiber length ($L_n$) versus feed rate for GF/PET composites

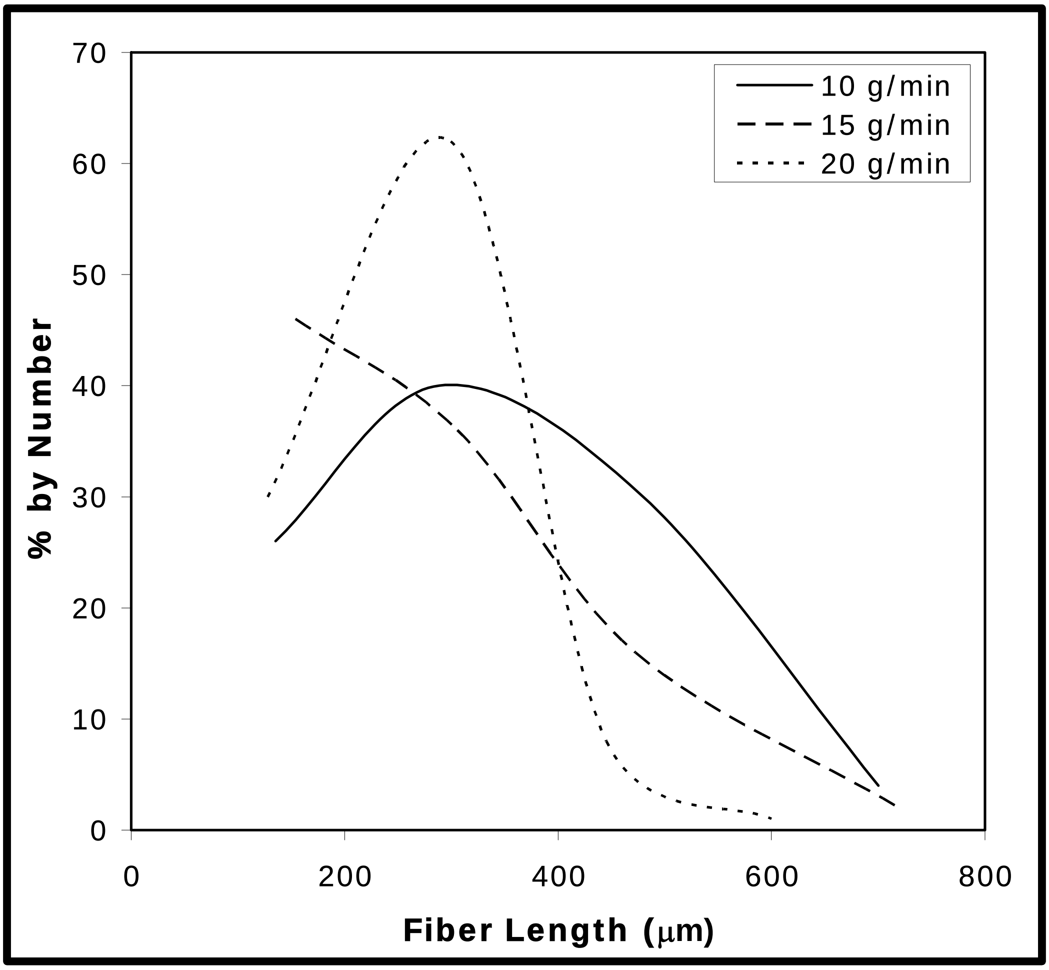


**Figure 4.25** Fiber length distribution of the GF/PET composites at various feed rates(g/min)

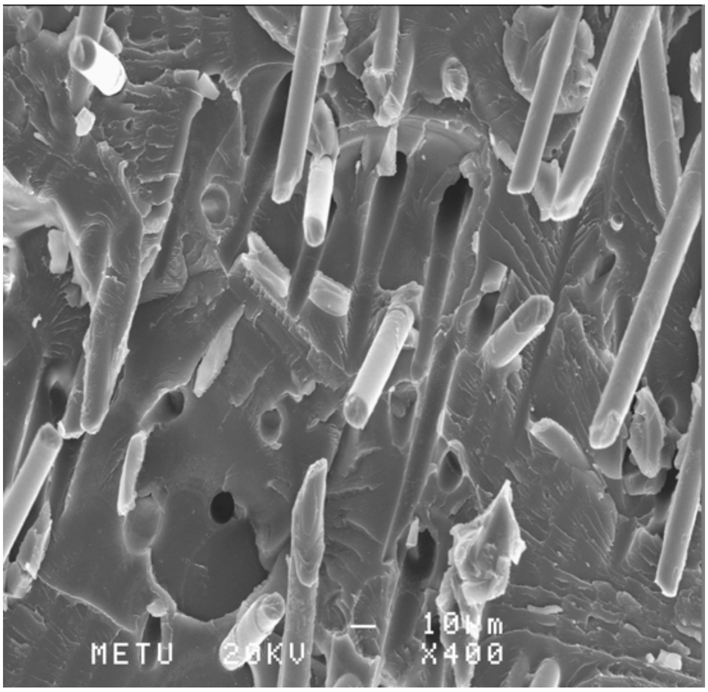
## 4.3 Effects of Silane Coupling Agents on Morphological, Thermal and Mechanical Properties of GF/PET Composites

Glass fibers are produced with consecutive operations. High quality glass in melt form is drawn from high-temperature alloy (bushing) tips at high cooling rates linearly meeting with water spray. Every fiber in unique composition with a diameter of 10.5, 13, 16μm (varies) pass across an application roll where they are coated with sizing solutions. Coated fibers are rolled on a collet and for curing they are put into furnaces at approximately $130^0$C for 14-16 hours. After curing it is hard to treat the glass fiber again. For successfull treatment, the organics (such as coupling agents) of the glass fibers, as received from manufacturer, must be driven out and then they could be applied by another sizing again. Also this procedure has some difficulties. While igniting the present organics, film formers are ignited too, this changes the form of glass fibers from slippery to bulky form. This makes impossible to coat virgin glass fibers with another coupling agent again. Based on this explanation, glass fibers which are received from the manufacturer, are treated without any ignition of present organics in order to observe the effects of treatment method and different coupling agents on the morphological, thermal and mechanical behavior of treated glass fiber/PET composites. Constant composition of %30GF/%70PET and constant process parameters such as screw speed of 230rpm and feed rate of 15rpm are applied during processing. Composition of the treated GF/PET composite and process parameters are selected according to the results given in Parts 4.1 and 4.2, by considering the optimum and/or reasonable mechanical properties of the composites.

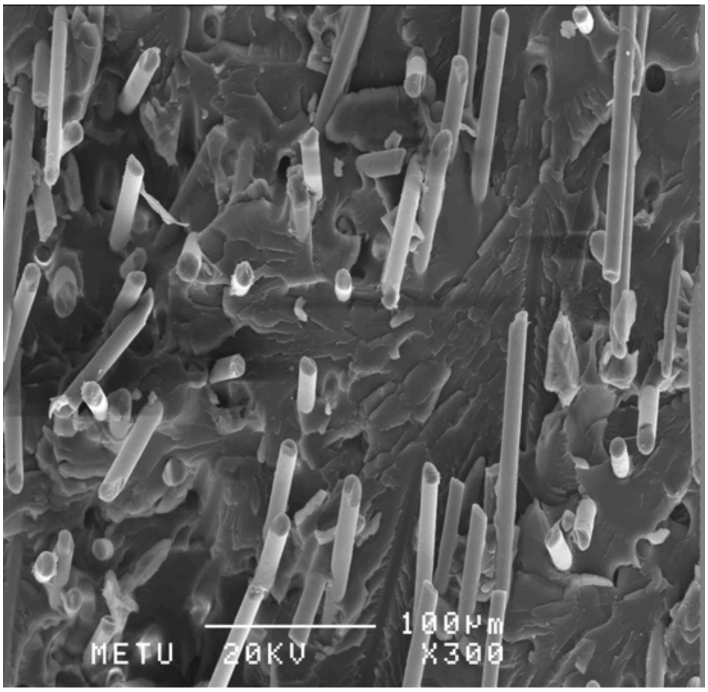
### 4.3.1 Scanning Electron Microscopy Analysis

The SEM micrographs of GF/PET composites with different types of coupling agents are shown in Figures 4.26 and 4.27.

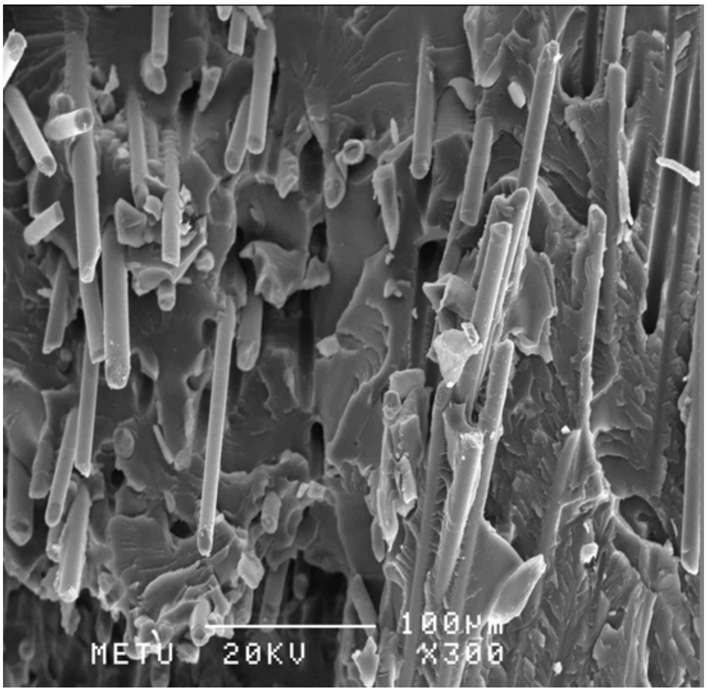
Figure 4.26a shows the SEM photograph of 3-APME treated GF/PET composite. Several holes are observed due to the pulled out glass fibers from the matrix, which are usuallly long and uncracked form. It can be said that the interaction between the glass fiber and PET matrix is weak. As the surface of the received glass fiber having 3-APE is covered by a 3-APME type of coupling agent, the functional groups of 3-APME may react with the functional groups of 3-APE. This reduces the bonding between the functional groups of coupling agent and PET. In the Figures 4.26 b,c and d, which show the SEM micrographs of N-B-3AM, 3-APE and 3-GPM treated GF/PET composites, it is hard to observe that the fibers are pulled out from the matrix indicating the existence of relatively stronger adhesion for silane coupling agents.



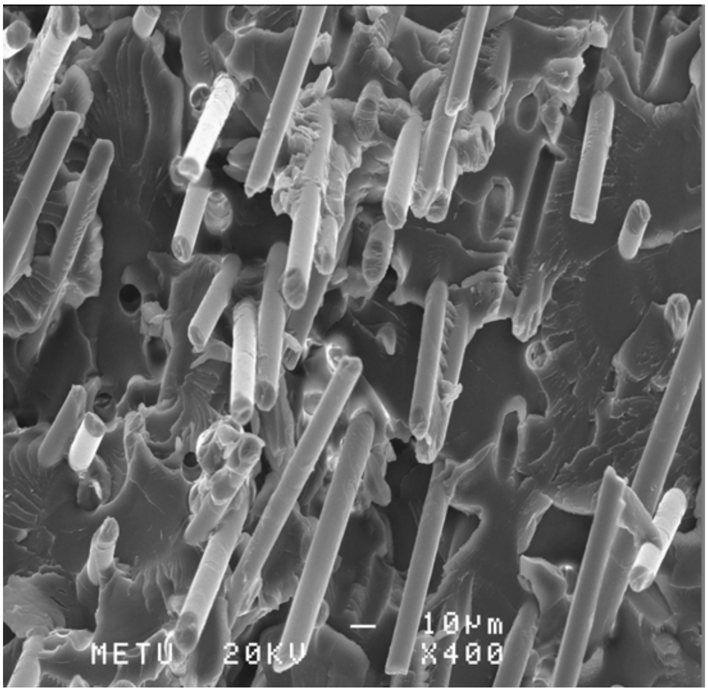
(a) GF/PET composite with 3-APME



(b) GF/PET composite with N-B-3-APM



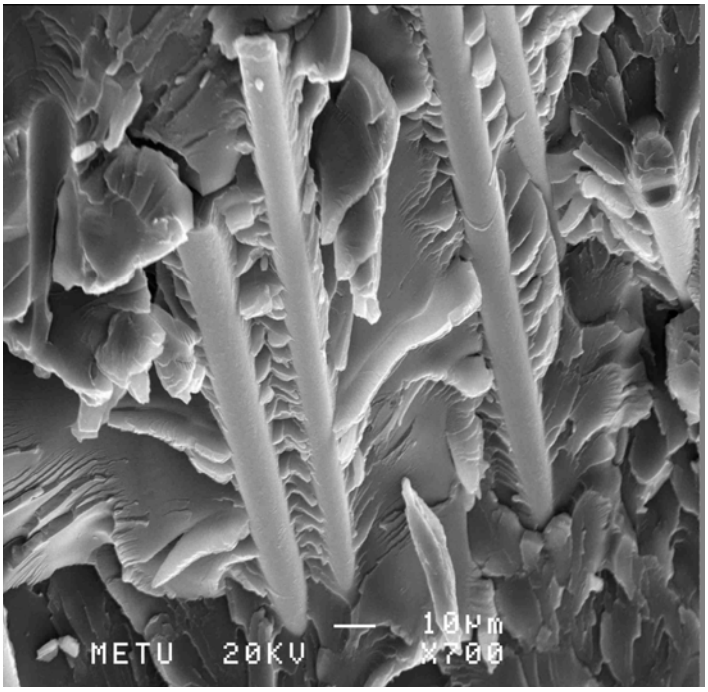
(c) GF/PET composite with 3-APE



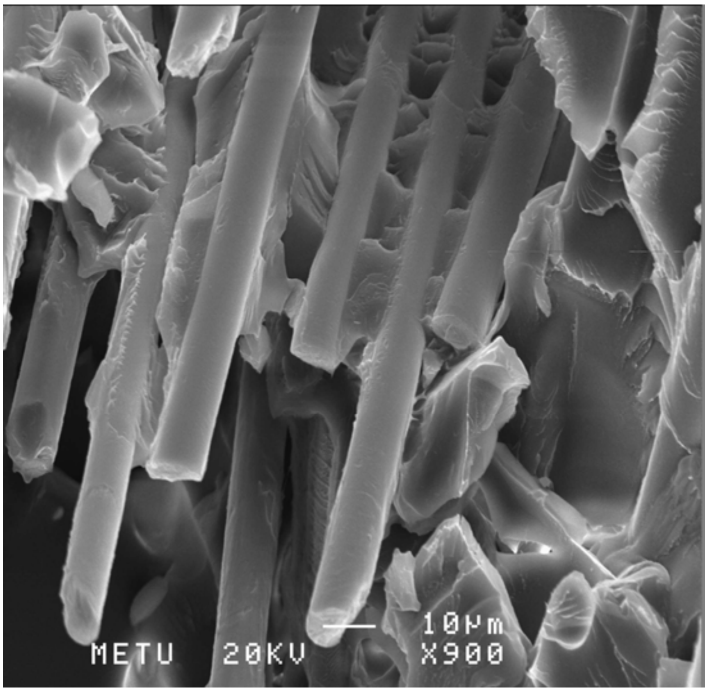
(d) GF/PET composite with 3-GPM

**Figure 4.26** SEM micrographs of GF/PET composites treated with different coupling agents a)3-APME, b)N-B-3-APM, c)3-APE and d)3-GPM (x300 and x400 magnifications)

Coupling agent reacts with the glass fiber surface by using hydrogen and covalent bonds between the hydroxyl groups of the fiber surface and the hydroxyl groups of the silane, and a chemical interaction takes place between the primary amino groups of the silane and the carboxylic groups of the PET. The use of the coupling agents which has epoxy group as functionality improves the interfacial adhesion betweeen glass fiber and polymer. This effect may be due to the chemical interaction between the functional group based on organic epoxide and the PET matrix. A strong adhesion between glass fiber and PET can be observed easily in the use of 3-GPM as coupling agent in Figures 4.26d and 4.27b. In the case of 3-APE as the coupling agent (Figure 4.28a), there is an enhancement of the interfacial bonding which increases the efficient stress transfer from PET to the glass fiber.



(a) GF/PET composite with 3-APE



(b) GF/PET composites with 3-GPM

**Figure 4.27** SEM micrographs of interfacial adhesion between treated glass fiber and PET a)3-APE and b)3-GPM

### 4.3.2 Differential Scanning Calorimetry Analysis

Table 4.5 shows the thermal properties and also % crystallinity of the treated GF/PET composites (See representative DSC thermograms in A.3). The glass transition temperatures of treated GF/PET composites with the coupling agents 3-APME and 3-GPM respectively decreased with respect to that of pure PET. The use of coupling agents, N-B-3-APM and 3-APE did not affect the $T_g$ significantly.

Additionally, a considerable change in the crystallinity is observed with the use of different coupling agents in chosen compositions with that of recycled PET. Although high crystallinity of polymers increases the stiffness and strength, it also introduces a brittle structure that results in some difficulties during processing. The observed changes in the % crystallinity can be explained in terms of the reduced influence of the reorganization process on the melting behavior [20]. The variation in the crystallinity values may be attributed to some chemical changes occurring as a consequence of the thermal treatment during DSC measurements. A thermal degradation on the sizing or a reaction between sizing components and PET are possible alternatives.

**Table 4.7** DSC results for GF/PET composites with different types of coupling agents

| **Material** | **$T_g$, PET ( $^oC$ )** | **$T_m$, PET ( $^oC$ )** | **$\Delta H_m$, PET ( J / gr PET )** | **% Crystallinity** |
|---|---|---|---|---|
| **PURE RPET** | 81.15 | 254.51 | 23.23 | 16.8 |
| **3-APME** | 72.25 | 252.90 | 37.30 | 27.0 |
| **N-B-3-APM** | 78.82 | 254.31 | 32.67 | 23.7 |
| **3-APE** | 77.72 | 254.26 | 32.13 | 23.3 |
| **3-GPM** | 76.36 | 253.89 | 43.40 | 31.4 |

### 4.3.3 Tensile Tests

Figure 4.28 shows the stress-strain curves for the composites treated with different coupling agents. The tensile strength, tensile (Young's) modulus and strain at break (% elongation) values with respect to different types of coupling agents are shown in Figures 4.29 through 4.31.

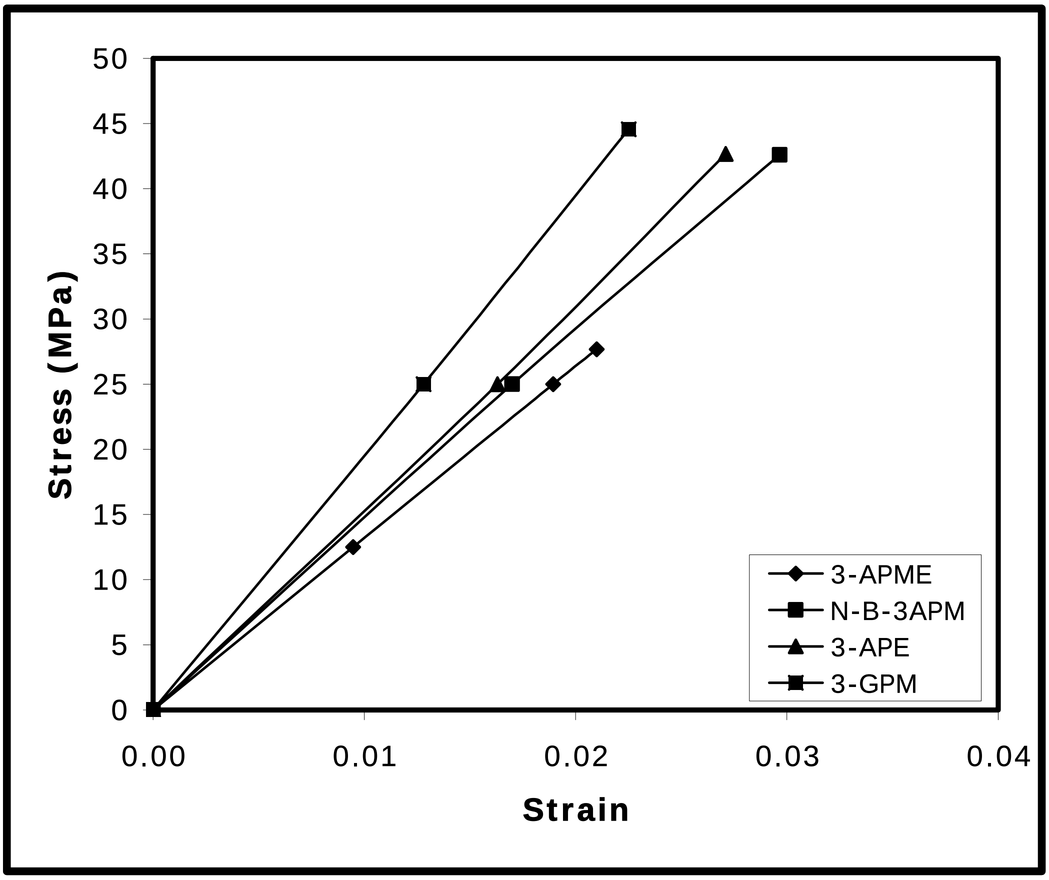


**Figure 4.28** Stress-Strain curves for 30% GF/70% PET composites treated with different coupling agents

#### 4.3.3.1 Tensile Strength

The tensile strength values of treated GF/PET composites with different types of coupling agents are presented in Figure 4.29. Since the interfacial adhesion between glass fiber and PET is much higher in coupling agents; N-B-3-APM, 3-APE and 3-GPM, tensile strength values of composites made from them are also higher. The composite with 3-APME coupling agent has a lower tensile strength in contrary to the others due to less interaction between the glass fiber and the matrix. Therefore as expected, in the use of this coupling agent hydrogen bonding does not occur between the components. Another reason for low tensile strength may be the deformation of the original sizing on the received glass fiber during the fiber treatment process.

#### 4.3.3.2 Tensile (Young’s) Modulus

An increasing trend of Tensile Moduli can be obtained by using coupling agents, 3-APE and 3-GPM as can be seen in Figure 4.30. Low tensile modulus value due to less interaction between the coupling agent 3-APME and PET matrix is also seen from the same figure. On the other hand, the lower value of tensile modulus for N-B-3-APM is somewhat unexpected. This can be due to decrease in hydrogen bonding upon degradation occurring in the system.

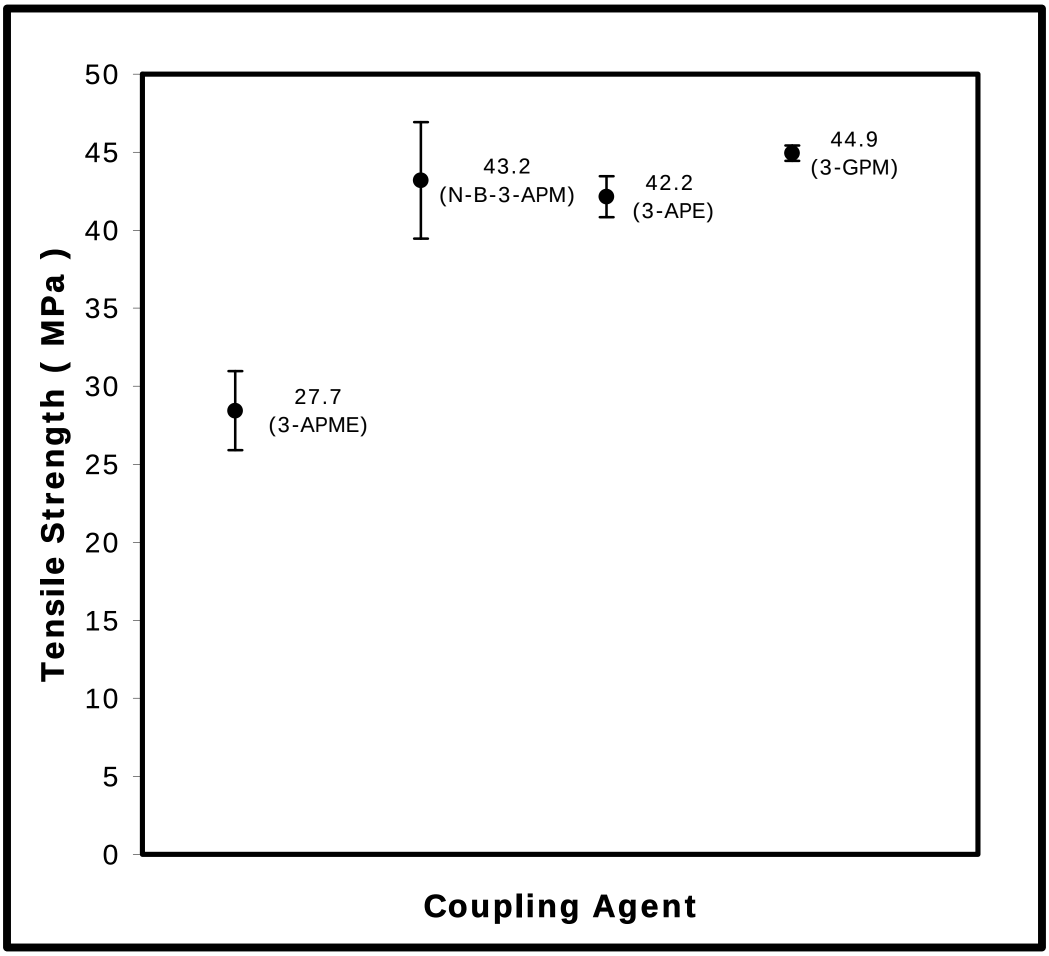


**Figure 4.29** Tensile Strength (MPa) versus coupling agents for 30% GF/70% PET composites

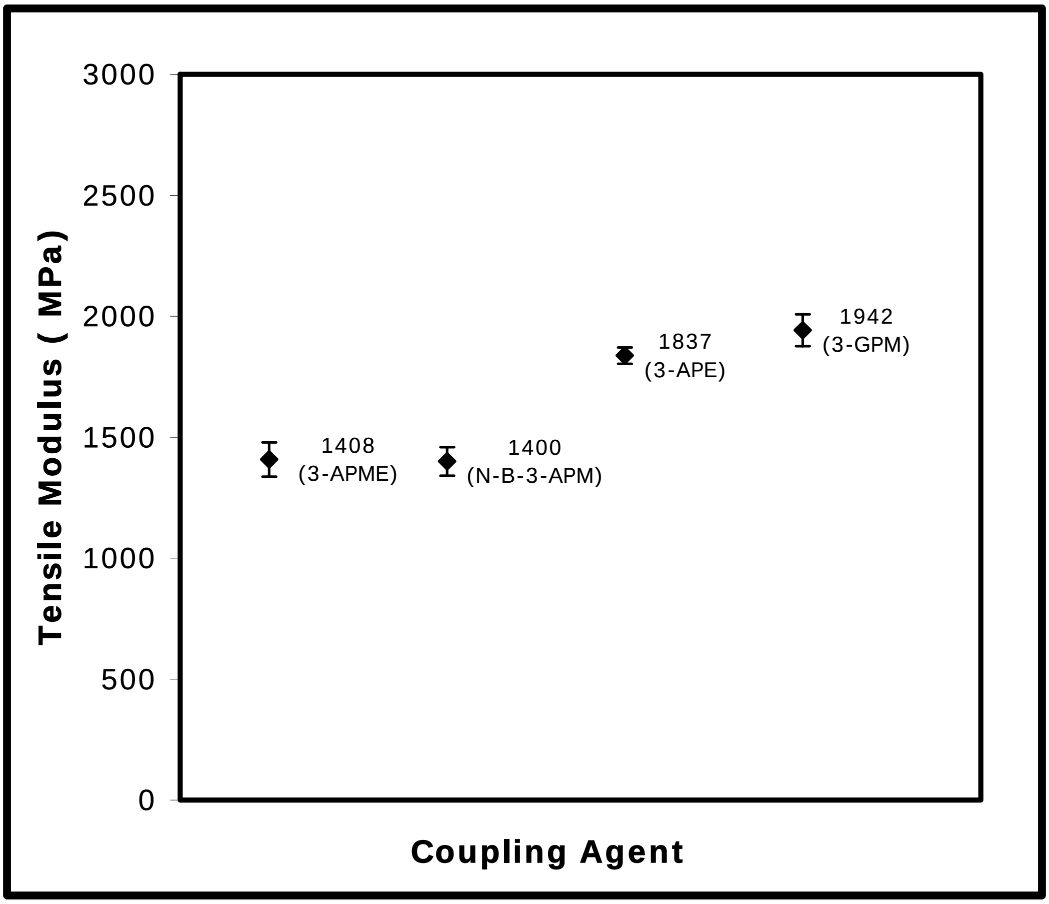


**Figure 4.30** Tensile Modulus (MPa) versus coupling agents for 30% GF/70% PET composites

#### 4.3.3.3 Strain at Break (% Elongation)

Strain at break values with respect to the different coupling agents are given in Figure 4.31. The retreatment of glass fibers with different types of coupling agents do not affect % elongation at break values of the composites significantly except the use of N-B-3-APM. The higher strain at break value of the GF/PET composite with N-B-3-APM can be attributed to the degradation occurring during fiber treatment process. As a result, the composite may have relatively high % elongation value.

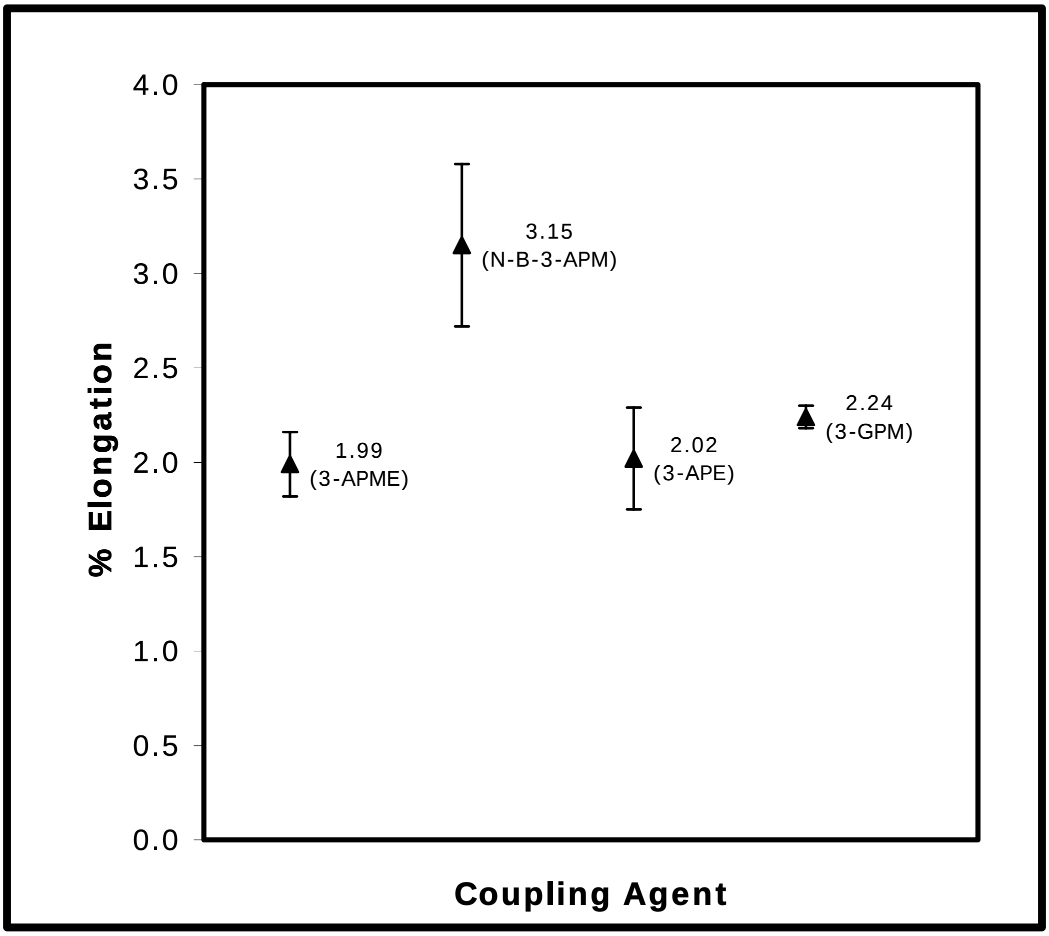


**Figure 4.31** % elongation versus coupling agent for 30% GF/70% PET composites

### 4.3.4 Ignition Tests

#### 4.3.4.1 Glass Fiber Content

Table 4.8 shows the results of glass fiber content obtained from ignition tests in the GF/PET composites and the original composition of the fibers in the composites which is adjusted before extrusion. In general, glass fiber concentrations in the treated GF/PET composites obtained from the tests are approximately 5-10% less than the original values. This may be due to decrease in the slippery property of the glass fibers during fiber treatment process and they may be more damaged during the extrusion. Another reason may be non-uniform feeding of glass fiber in the extrusion, therefore glass fiber content in the composite is lower than the original ones.

**Table 4.8** Glass fiber content in the GF/PET composites treated with different coupling agents

| Planned GF Content; (30%) | Obtained GF Content |
|---|---|
| 3-APME | 25.2% |
| N-B-3-APM | 25.5% |
| 3-APE | 20.7% |
| 3-GPM | 26.3% |

#### 4.3.4.2 Fiber Length Distribution

Number average fiber length and fiber length distributions with respect to types of coupling agent are shown in Figures 4.32 and 4.33. The corresponding data for in these figures are shown in Table A.2.

Figure 4.32 shows that the composite having N-B-3-APM coupling agent has a maximum value in number average fiber length among the other silane coupling agents. The glass fiber-polymer matrix is influenced by shearing stress during extrusion which results in a decrease in tensile strength due to decrease in fiber length (Figure 4.29). Since the use of N-B-3-APM and 3-APE affect positively the interfacial adhesion between fiber and PET, the fiber is not affected much by the shear stress during extrusion. Therefore, reduction in fiber length is less than the others. In tensile properties, the effects of both fiber length and interaction between the fiber and the matrix, compete each other. Even though the number average fiber length is low, there may be high values of tensile properties due to the improved adhesion between the components of the composites.

Figure 4.33 shows that fiber length distribution of the composite with 3-APE is broader than the other ones. This may support its high tensile strength and modulus values over the composites containing 3-APME and N-B-3-APM.

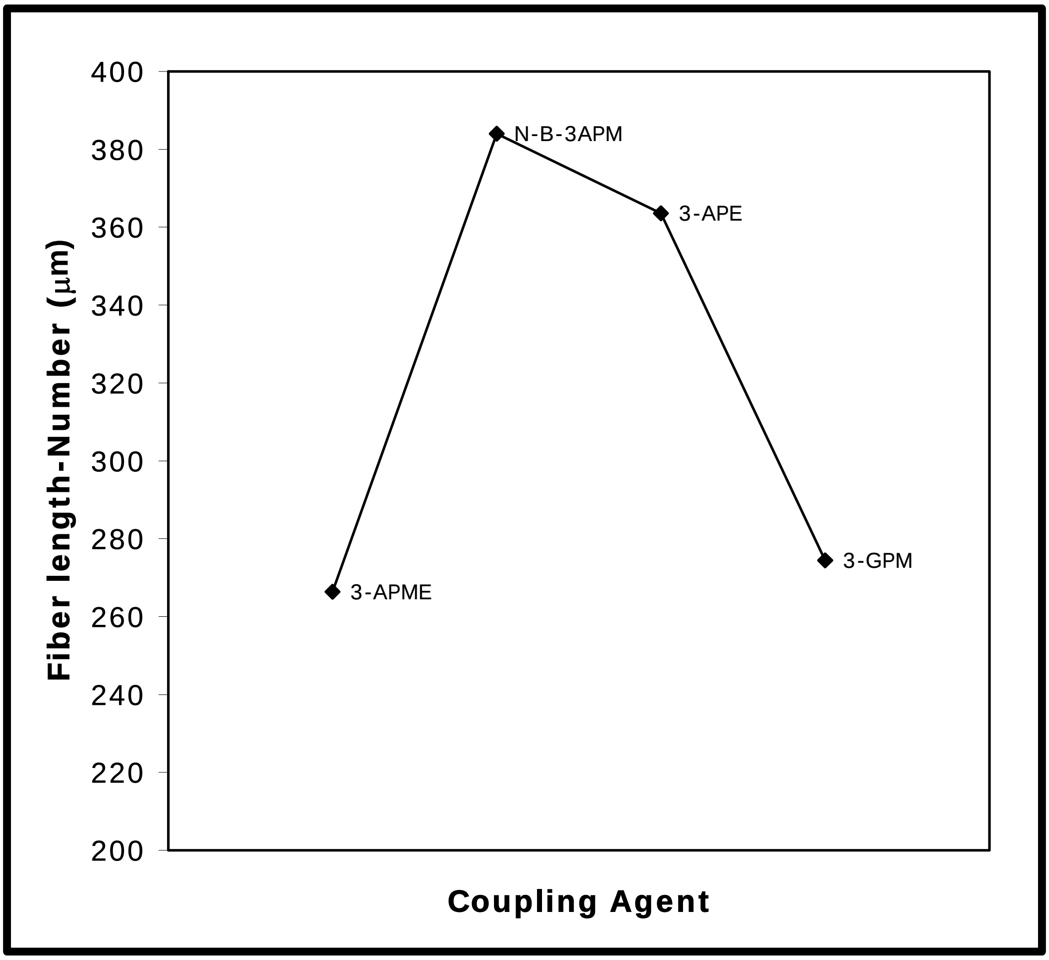


**Figure 4.32** Number average fiber length ($L_n$) versus coupling agent for 30% GF/70% PET composites

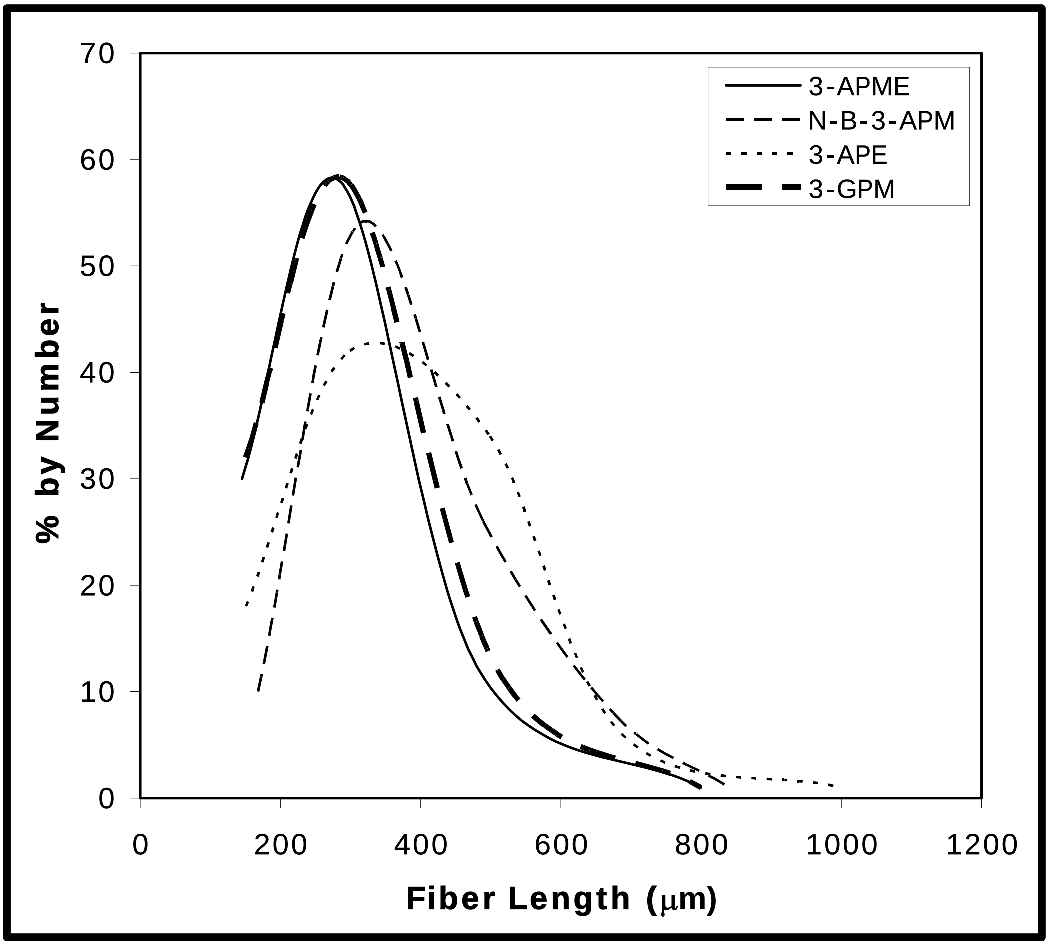


**Figure 4.33** Fiber length distribution at different coupling agents

# CHAPTER V

# CONCLUSIONS

In this study, glass fiber/PET composites were produced using a twin screw extruder. Effects of glass fiber concentration, process parameters and silane coupling agents on final properties of the composites were studied. It was found that 30% GF concentration of the composite with processing parameters of 230rpm screw speed and 15g/min feed rate were the optimum conditions of this study among the parameters studied. When the types of different silane coupling agents were concerned, 3-GPM type coupling agent seems to be a promising one for further studies due to its high reaction capability with PET and glass fiber.

The tensile properties of PET were improved in the presence of glass fibers. As glass fiber content increased, tensile strength and tensile (Young's) moduli values of the composites increased. Tensile strength showed a maximum at 45% glass fiber/55% PET composite composition. With further addition of glass fiber (at 55%) a lower tensile strength was obtained due to excess fiber/fiber interaction rather than the interaction between the glass fiber and the PET.

It was seen from SEM micrographs, that the interfacial adhesion between glass fiber received from the manufacturer and the PET is good. Interfacial adhesion increased with increasing amount of glass fiber content which provides high stress transfer from PET to glass fiber.

Increasing screw speed did not affect the tensile strength and the moduli of the composites significantly. Increasing feed rate decreased the tensile strength because of high shearing and showed a maximum in tensile modulus values.

Effects of functional groups of coupling agents on interfacial adhesion between glass fiber and PET were studied by SEM analysis and tensile tests. The coupling agent 3-APME which has less effective functional groups than the others exhibited poor adhesion between glass fiber and polymer, which also resulted in low values in tensile properties of the 3-APME containing composite.

Thermal properties of the composites were analyzed by DSC. Melting point temperature of the composites did not change significantly, but, % crystallinity values were drastically affected by the change in glass fiber concentration, process parameters and the type of silane coupling agents.

Measurements of fiber length distribution showed that number average fiber length was reduced from 4.5mm to approximately 300μm for almost all the composites prepared in this study.

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# APPENDICES

## A.1 Tensile Test Results for All Samples

**Table A.1.1** Data for representative stress-strain curves

| GF Content | Stress (Mpa) | Strain |
|---|---|---|
| 10% | | |
| | 0.00 | 0.000 |
| | 12.50 | 0.016 |
| | 25.00 | 0.029 |
| | 37.50 | 0.045 |
| | 42.74 | 0.052 |
| 15% | | |
| | 0.00 | 0.000 |
| | 12.50 | 0.012 |
| | 25.00 | 0.021 |
| | 37.50 | 0.037 |
| | 42.79 | 0.043 |
| 30% | | |
| | 0.00 | 0.000 |
| | 18.75 | 0.014 |
| | 37.50 | 0.031 |
| | 56.25 | 0.046 |
| | 59.42 | 0.499 |
| 45% | | |
| | 0.00 | 0.000 |
| | 25.00 | 0.015 |
| | 50.00 | 0.034 |
| | 75.00 | 0.046 |
| | 73.95 | 0.058 |
| 55% | | |
| | 0.00 | 0.000 |
| | 18.75 | 0.009 |
| | 37.50 | 0.018 |
| | 56.25 | 0.030 |
| | 57.87 | 0.031 |

## Table A.1.1 Continuation from page 111

| **Screw Speed** | **Stress (MPa)** | **Strain** |
|---|---|---|
| 170 rpm | | |
| | 0 | 0 |
| | 25 | 0.017 |
| | 50 | 0.0355 |
| | 60.73 | 0.0447 |
| 230 rpm | | |
| | 0 | 0 |
| | 18.75 | 0.0139 |
| | 37.5 | 0.0308 |
| | 59.42 | 0.4990 |
| 290 rpm | | |
| | 0 | 0 |
| | 25 | 0.0220 |
| | 50 | 0.0497 |
| | 58.77 | 0.0581 |
| **Feed Rate** | **Stress (MPa)** | **Strain** |
| 10 g/min | | |
| | 0 | 0 |
| | 25 | 0.0137 |
| | 50 | 0.0317 |
| | 71.54 | 0.0515 |
| 15 g/min | | |
| | 0 | 0 |
| | 25 | 0.0168 |
| | 50 | 0.0331 |
| | 68.07 | 0.0502 |
| 20 g/min | | |
| | 0 | 0 |
| | 18.75 | 0.0139 |
| | 37.5 | 0.0308 |
| | 59.42 | 0.4990 |

## Table A.1.1 Continuation from page 112

| Coupling Agent | Stress (MPa) | Strain |
|---|---|---|
| 3-APME | | |
| | 0 | 0 |
| | 12.5 | 0.00947 |
| | 25 | 0.01894 |
| | 27.66 | 0.021 |
| N-B-3-APM | | |
| | 0 | 0 |
| | 25 | 0.0170 |
| | 42.59 | 0.0297 |
| 3-APE | | |
| | 0 | 0 |
| | 25 | 0.0163 |
| | 42.67 | 0.0271 |
| 3-GPM | | |
| | 0 | 0 |
| | 25 | 0.0128 |
| | 44.57 | 0.0225 |

**Table A.1.2** Data for tensile strength

| | **Tensile Strength (Mpa)** | **Std.Dev.** |
|---|---|---|
| **GF Content** | | |
| 10% | 42.74 | 4.31 |
| 15% | 42.79 | 4.04 |
| 30% | 59.42 | 4.21 |
| 45% | 73.95 | 1.74 |
| 55% | 57.87 | 2.23 |
| **Screw Speed** | | |
| 170 rpm | 59.68 | 3.52 |
| 230 rpm | 59.42 | 4.21 |
| 290 rpm | 59.98 | 4.56 |
| **Feed Rate** | | |
| 10 g/min | 68.98 | 5.34 |
| 15 g/min | 68.82 | 2.41 |
| 20 g/min | 59.42 | 4.21 |
| **Coupling Agent** | | |
| 3-APME | 28.43 | 2.53 |
| N-B-3-APM | 43.19 | 3.74 |
| 3-APE | 42.15 | 1.31 |
| 3-GPM | 44.93 | 0.49 |

**Table A.1.3** Data for tensile (Young's) modulus

| | **Tensile Modulus (Mpa)** | **Std.Dev.** |
|---|---|---|
| **GF Content** | | |
| 10% | 903.1 | 121.43 |
| 15% | 1312.25 | 155.34 |
| 30% | 1644.39 | 98.47 |
| 45% | 1903.25 | 114.17 |
| 55% | 1913.2 | 294.43 |
| **Screw Speed** | | |
| 170 rpm | 1896.33 | 73.44 |
| 230 rpm | 1644.39 | 98.47 |
| 290 rpm | 1621.17 | 113.42 |
| **Feed Rate** | | |
| 10 g/min | 1685.44 | 186.04 |
| 15 g/min | 1940.43 | 116.89 |
| 20 g/min | 1644.39 | 98.47 |
| **Coupling Agent** | | |
| 3-APME | 1407.85 | 70.39 |
| N-B-3-APM | 1399.92 | 58.89 |
| 3-APE | 1837.24 | 33.95 |
| 3-GPM | 1941.93 | 66.29 |

**Table A.1.4** Data for strain at break (% Elongation)

| | **% Elongation** | **Std.Dev.** |
|---|---|---|
| **GF Content** | | |
| 10% | 4.95 | 0.53 |
| 15% | 2.85 | 0.64 |
| 30% | 4.99 | 0.31 |
| 45% | 5.63 | 0.28 |
| 55% | 3.1 | 0.2 |
| **Screw Speed** | | |
| 170 rpm | 3.41 | 0.35 |
| 230 rpm | 4.99 | 0.31 |
| 290 rpm | 3.69 | 0.28 |
| **Feed Rate** | | |
| 10 g/min | 3.74 | 0.32 |
| 15 g/min | 4 | 0.52 |
| 20 g/min | 4.99 | 0.31 |
| **Coupling Agent** | | |
| 3-APME | 1.99 | 0.17 |
| N-B-3-APM | 3.15 | 0.43 |
| 3-APE | 2.02 | 0.27 |
| 3-GPM | 2.24 | 0.06 |

## A.2 Fiber Length Distribution Results for All Samples

**Table A.2.1** Data for number average fiber length

| | **Number Average Fiber Length ($L_n$)** |
|---|---|
| **GF Content** | |
| 10% | 320 |
| 15% | 299.5 |
| 30% | 259.6 |
| 45% | 272.5 |
| 55% | 338.8 |
| **Screw Speed** | |
| 170 rpm | 377.6 |
| 230 rpm | 259.6 |
| 290 rpm | 374.8 |
| **Feed Rate** | |
| 10 g/min | 322.8 |
| 15 g/min | 270.8 |
| 20 g/min | 259.6 |
| **Coupling Agent** | |
| 3-APME | 266.4 |
| N-B-3-APM | 384 |
| 3-APE | 363.6 |
| 3-GPM | 274.4 |

**Table A.2.2** Data for fiber length distribution

Number of fibers by % versus number average fiber length for GF/PET composites with different amount of glass fibers

| **10% GF** | **%** | **15% GF** | **%** | **30% GF** | **%** | **45% GF** | **%** | **55% GF** | **%** |
|---|---|---|---|---|---|---|---|---|---|
| 117 | 34 | 143 | 31.5 | 128 | 29 | 143 | 45 | 140 | 51.3 |
| 273 | 37 | 282 | 42.5 | 300 | 62 | 284 | 36.5 | 295 | 37.5 |
| 464 | 23 | 480 | 17.5 | 445 | 8 | 520 | 10 | 530 | 5.1 |
| 673 | 5 | 653 | 7.5 | 600 | 1 | 660 | 7.5 | 670 | 5.1 |
| 800 | 1 | 800 | 1 | 800 | 0 | 800 | 1 | 800 | 1 |

Number of fibers by % versus number average fiber length for GF/PET composites at different screw speeds

| **170 rpm** | **%** | **230 rpm** | **%** | **290 rpm** | **%** |
|---|---|---|---|---|---|
| 191 | 15.7 | 128 | 29 | 147 | 21.6 |
| 322 | 49 | 300 | 62 | 310 | 41.2 |
| 506 | 31.4 | 445 | 8 | 492 | 21.6 |
| 690 | 3.9 | 600 | 1 | 663 | 11.7 |
|  |  |  |  | 860 | 3.9 |

Number of fibers by % versus number average fiber length for GF/PET composites at different feed rates

| **10 g/min** | **%** | **15 g/min** | **%** | **20 g/min** | **%** |
|---|---|---|---|---|---|
| 135 | 26 | 154 | 46 | 128 | 29 |
| 289 | 40 | 306 | 36 | 300 | 62 |
| 480 | 30 | 473 | 16 | 445 | 8 |
| 700 | 4 | 720 | 2 | 600 | 1 |

Number of fibers by % versus number average fiber length
for GF/PET composites with different coupling agents

| **3-APME** | **%** | **N-B-3-APM** | **%** | **3-APE** | **%** | **3-GPM** | **%** |
|---|---|---|---|---|---|---|---|
| 145 | 29 | 168 | 11 | 151 | 18 | 150 | 31 |
| 284 | 58 | 313 | 54 | 300 | 42 | 295 | 57 |
| 483 | 12 | 489 | 26 | 499 | 33 | 510 | 11 |
| 800 | 1 | 675 | 8 | 687 | 6 | 800 | 1 |
|  |  | 840 | 1 | 1000 | 1 |  |  |

## A.3 DSC thermograms of GF/PET composites

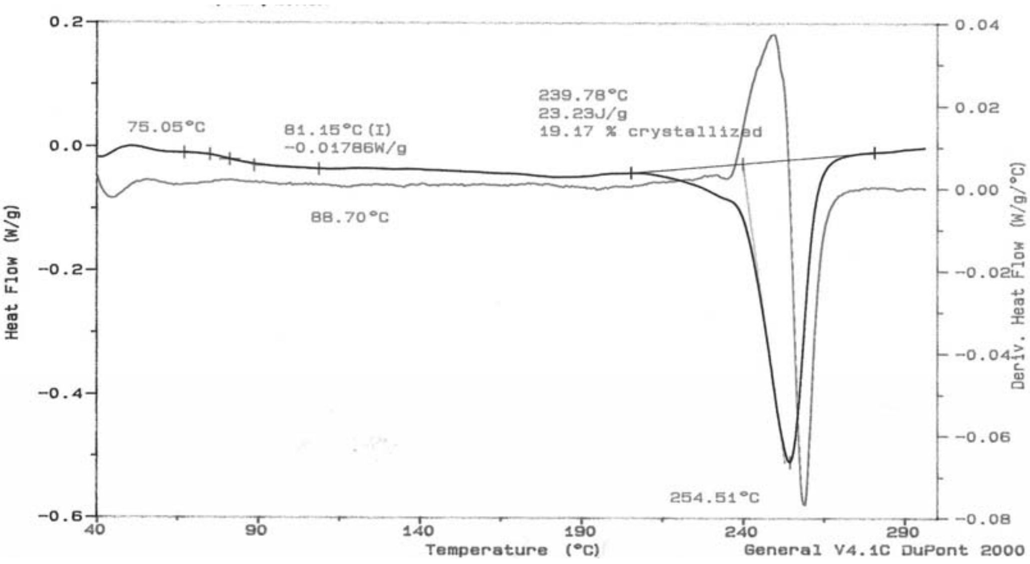

**Figure A.3.1** DSC thermogram of pure recycled PET

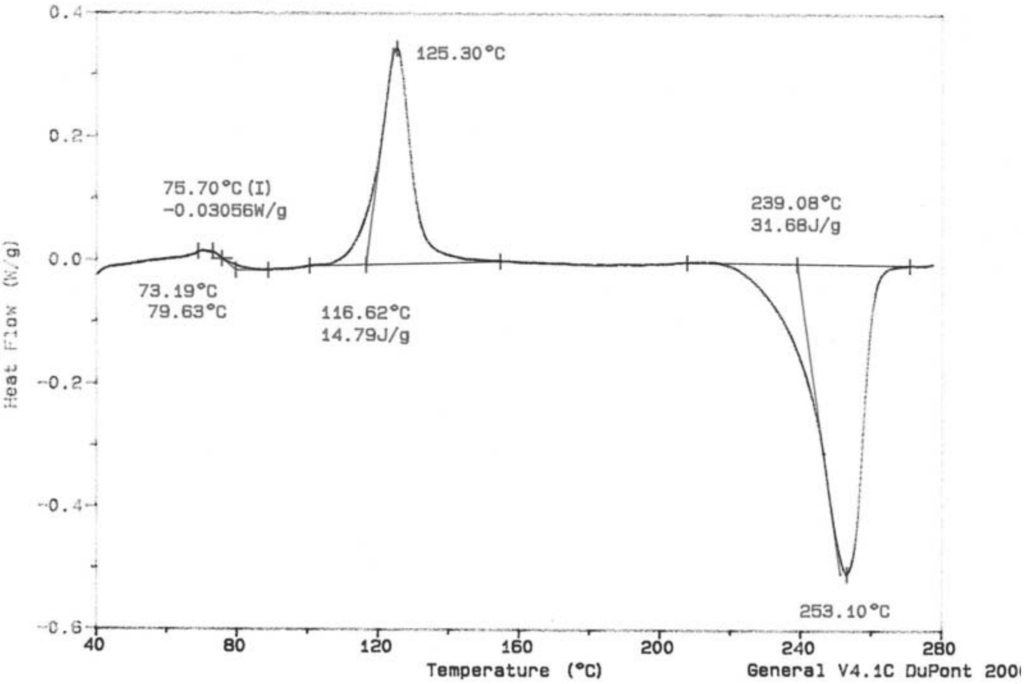

**Figure A.3.2** DSC thermogram of 30% GF/70% PET composite processed at screw speed of 170rpm and feed rate of 20g/min

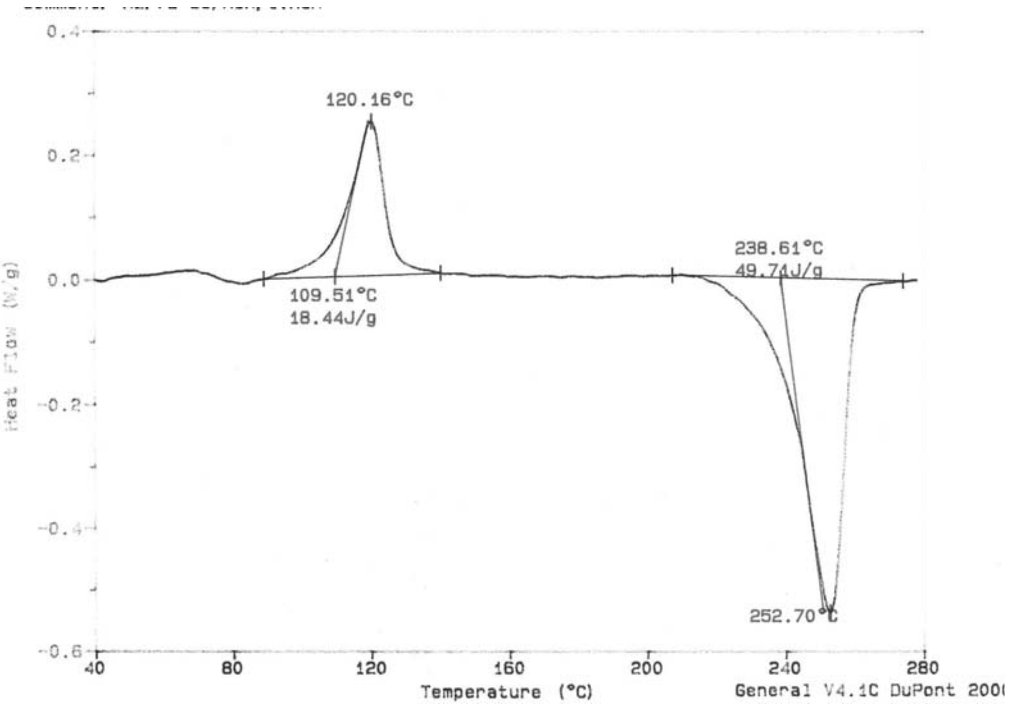

**Figure A.3.3** DSC thermogram of 30% GF/70% PET composite processed at screw speed of 230rpm and feed rate of 20g/min

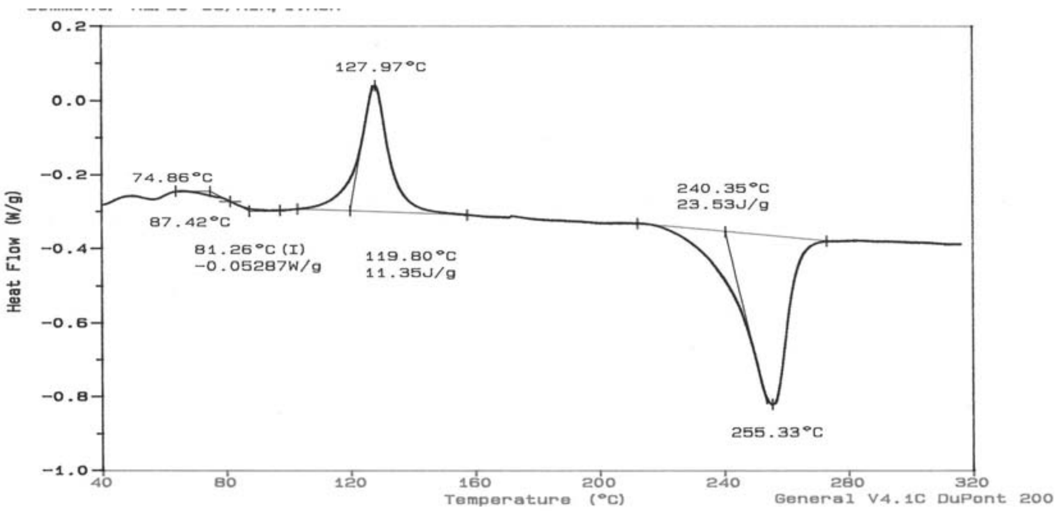

**Figure A.3.4** DSC thermogram of 30% GF/70% PET composite processed at screw speed of 290rpm and feed rate of 20g/min

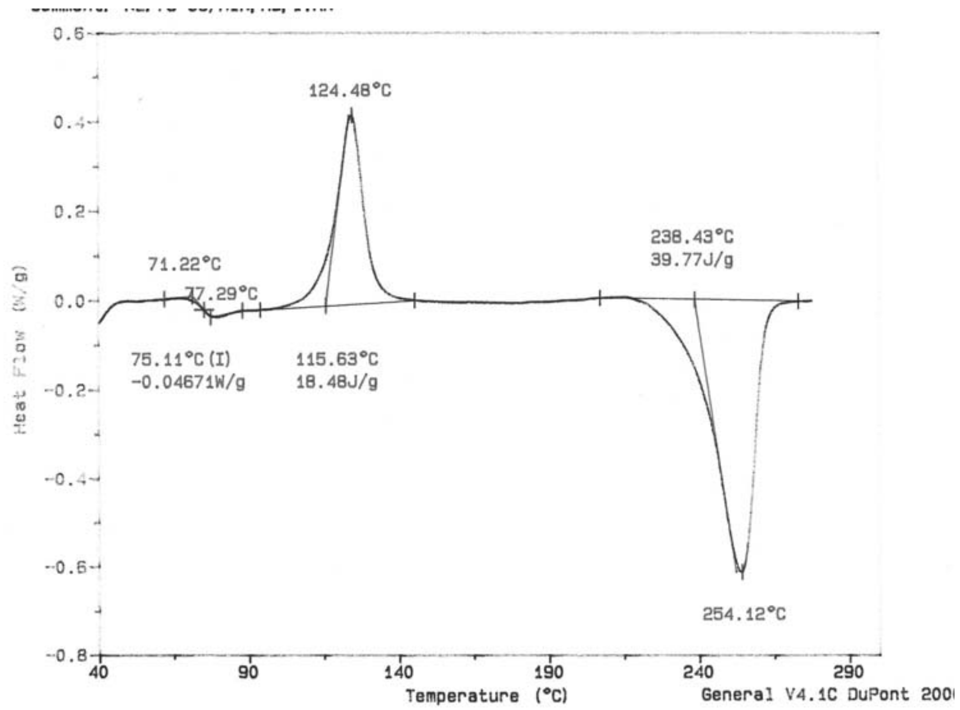

**Figure A.3.5** DSC thermogram of 30% GF/70% PET composite processed at screw speed of 230rpm and feed rate o

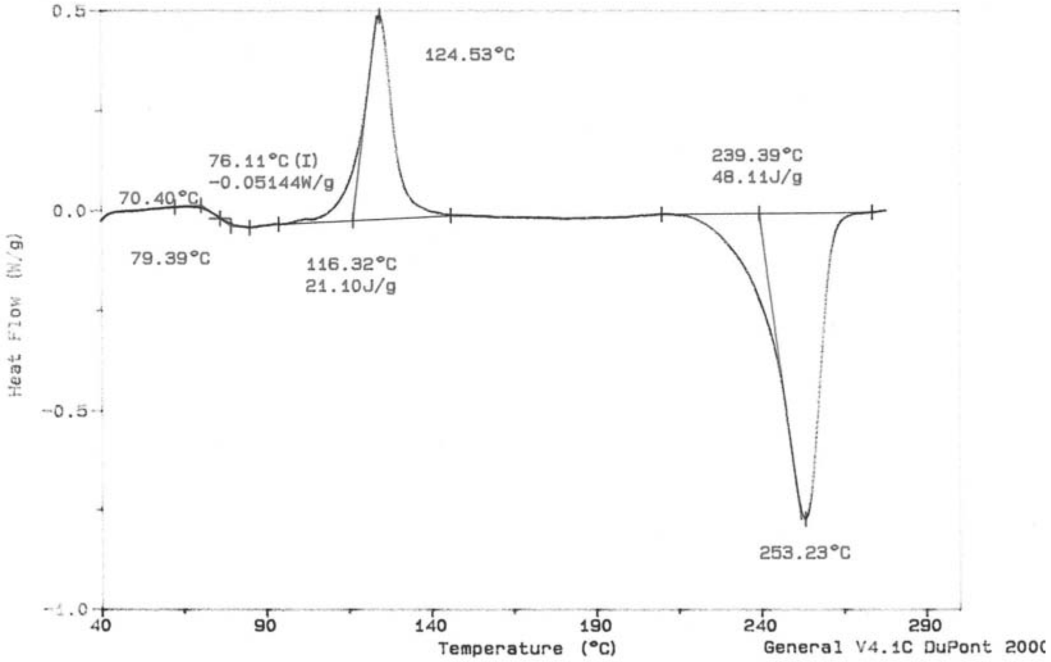

**Figure A.3.6** DSC thermogram of 30% GF/70% PET composite processed at screw speed of 230rpm and feed rate of 15g/min

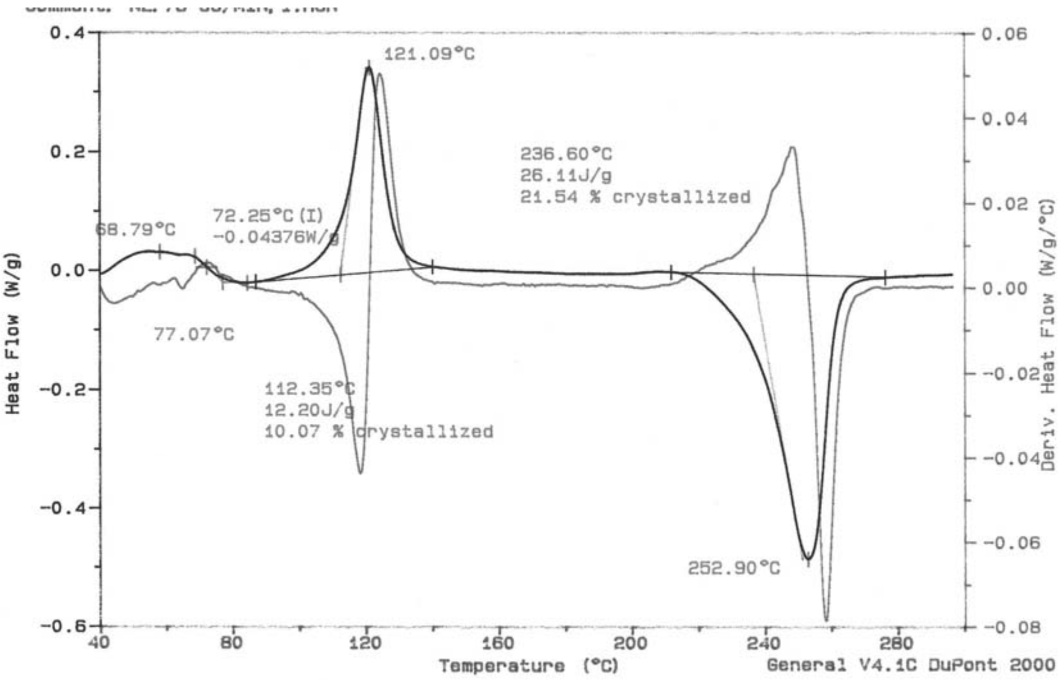

**Figure A.3.7** DSC thermogram of 30% GF/70% PET composite processed at screw speed of 230rpm and feed rate of 15g/min with the coupling agent of 3-APME

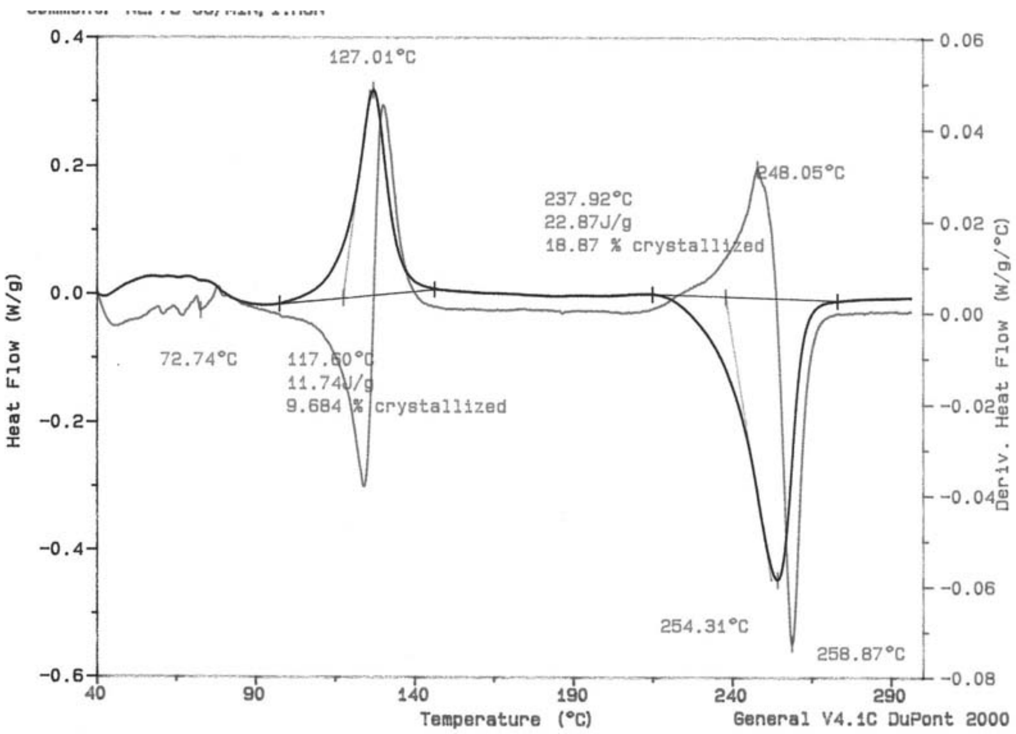

**Figure A.3.8** DSC thermogram of 30% GF/70% PET composite processed at screw speed of 230rpm and feed rate of 15g/min with the coupling agent of N-B-3-APM

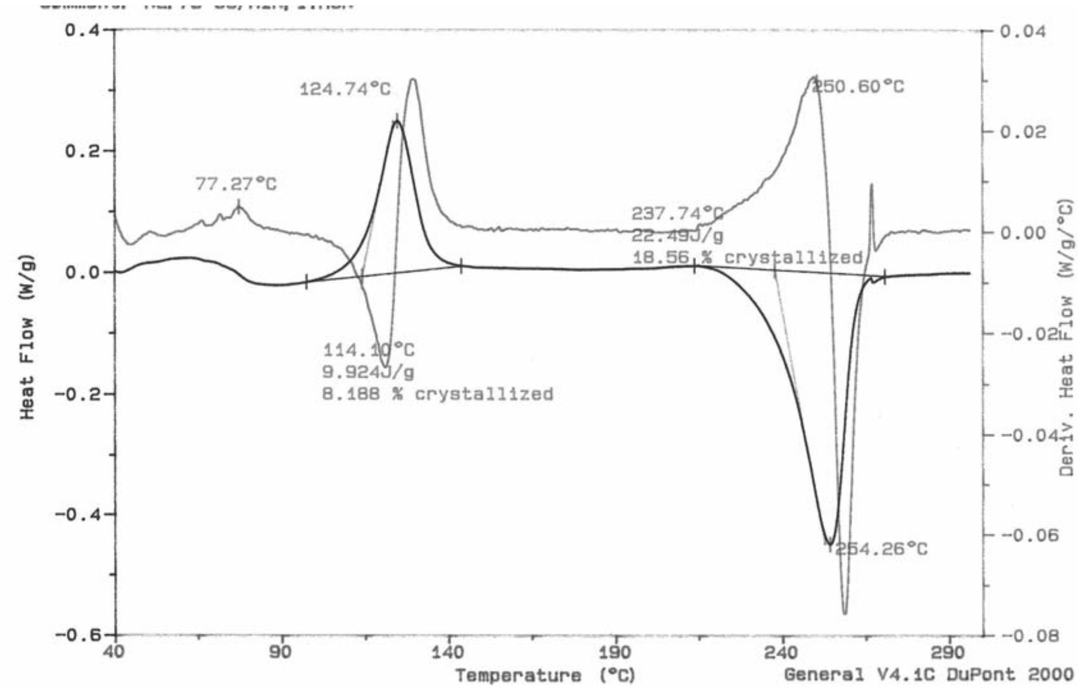

**Figure A.3.9** DSC thermogram of 30% GF/70% PET composite processed at screw speed of 230rpm and feed rate of 15g/min with the coupling agent of 3-APE

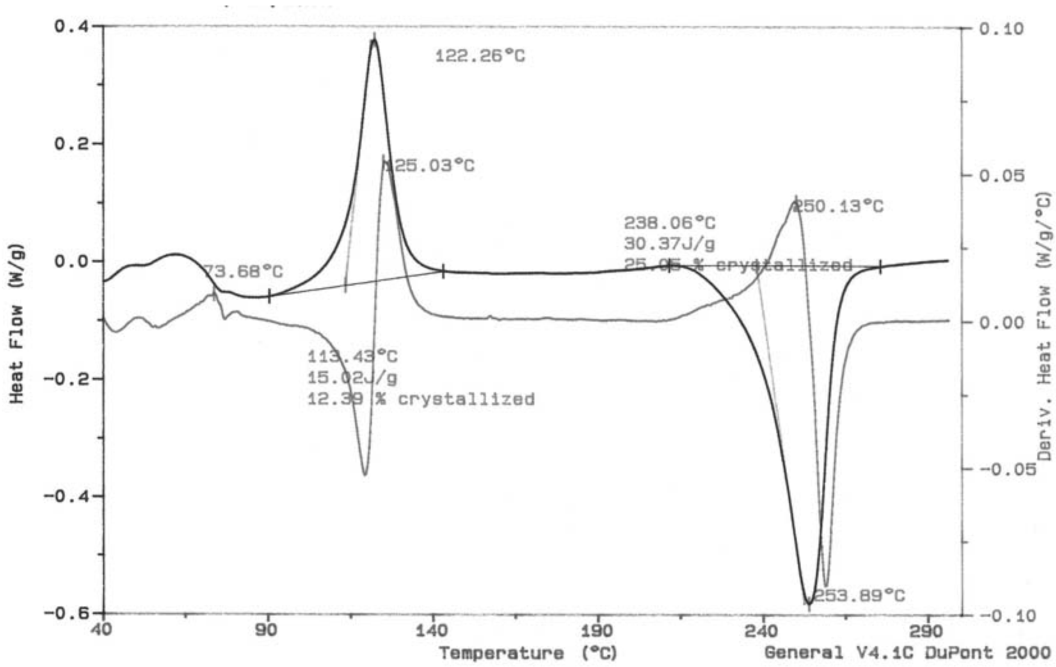

**Figure A.3.10** DSC thermogram of 30% GF/70% PET composite processed at screw speed of 230rpm and feed rate of 15g/min with the coupling agent of 3-GPM