Effect of Fluorination and Oxy-Fluorination of Kevlar Fiber on the Properties of Short Fiber Reinforced Polymer Composites and Its Mold Flow Simulation Study

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Madhumita Mukherjee

Under the Guidance of

Prof. C.K.Das



Materials Science Centre Indian Institute of Technology, Kharagpur Kharagpur – 721302 India

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Dedicated to Maa & Baba

Prof. C.K.Das Professor & Head

Certificate

This is to certify that the thesis entitled "Effect of Fluorination and Oxy-Fluorination of Kevlar Fiber on the Properties of Short Fiber Reinforced Polymer Composites and Its Mold Flow Simulation Study" is being submitted by Madhumita Mukherjee for the award of the degree of Doctor of Philosophy to the Indian Institute of Technology, Kharagpur, India, is a record of bonafide research work carried out by her under my direct supervision and guidance.

In my opinion, the thesis has fulfilled the requirements according to the regulations of this Institute and has reached the standard necessary for submission. The results presented in this thesis have not been submitted elsewhere for award of any other degree or diploma.

Prof. C. K. Das

Head of the Centre Materials Science Centre Indian Institute of Technology Kharagpur -721302, India

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Prefac	e
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Recently, much progress has been made in the development of reinforced composite materials because they have an outstanding combination of mechanical and physical properties. These composites, which include carbon, steel, and glass fibers embedded in a resin matrix, are currently playing a leading role in many advanced technological and constructional applications. Short fiber reinforcements are preferred over the continuous fiber reinforcement because of the combination of easier processability with low manufacturing cost. Kevlar fiber owing its high tenacity is a good candidate as the reinforcement for polymer composites. However, because of high crystallinity, surface of the Kevlar fiber is chemically inert and smooth, thus its adhesion with matrix is very much poor. Therefore, to use Kevlar fiber as reinforcement, surface modification is essential to enhance its reinforcing effects. The surface modification of Kevlar fiber must be chosen according to the corresponding resin matrix. Direct fluorination and oxy-fluorination has been successfully used to modify the fiber surface to improve the fiber/matrix adhesion. Simulation of fiber orientation as well as the processing conditions is very much important to predict the properties of the fiber reinforced composites.

The Thesis is divided into 7 Chapters

Chapter-1 includes the introduction in which first section, namely the background outline, the necessary links of the materials used. The next part covers the objectives and scope of the work.

Chapter-2 includes the details regarding the materials used and the experimental techniques followed in the present investigation.

Chapter-3A describes the effect of fluorinated and oxy-fluorinated short Kevlar fiber on the thermal, dynamic mechanical and crystalline properties of ethylene polypropylene copolymer matrix.

Chapter–3B deals with the compstibilizing effect of MA-g-PP on the thermal, dynamic, mechanical and crystalline properties of fluorinated and oxy-fluorinated short Kevlar fiber reinforced ethylene propylene matrix composites.

Chapter-3C highlights the influence of fluorinated and oxy-fluorinated short Kevlar fiber loading on the thermal, dynamic mechanical and crystalline properties of the ethylene polypropylene matrix composites.

Chapter-4A studies the thermal, dynamic mechanical and crystalline properties of the fluorinated and oxy-fluorinated short Kevlar fiber reinforced syndiotactic polystyrene composites

Chapter-4B deals with the rheological and mechanical properties of the oxy-fluorinated short Kevlar fiber reinforced polymer composites.

Chapter-5 highlights the effect of processing parameters on the thermal properties and simulation of fiber orientation of the fluorinated short

Kevlar fiber reinforced syndiotactic polystyrene composites using mold flow technique.

Chapter-6 deals with the thermal, dynamic mechanical, crystalline properties of the fluorinated and oxy-fluorinated short Kevlar fiber reinforced polycarbonate and liquid crystalline polymer blends including the simulation of fiber orientation of the same under different processing conditions.

Chapter-7 contains the summary and conclusions of the present work together with a glossary of the terms and references. Finally, the thesis is with the list of publications.



Thermoplastic-based composites are becoming more important in many application fields for the possibility of combination of toughness of thermoplastic polymers with stiffness and strength of reinforcing fibers. The ultimate properties of the composites solely depend on the characteristics features of fiber and matrix and on the adhesion strength at the interface. In order to massive and economical application matrix should be easily available, economic and well established. For that purpose ethylene polypropylene copolymer, syndiotactic polystyrene and polycarbonate have been chosen as the base matrix for the reinforced composites. Organic textile fibers can be used to prepare polymer composite. Due to their low stiffness organic textile fibers are used as reinforcing agent in polymer matrices, such as rubbers and thermoplastics. It is well known that behavior of the polymeric material strongly dependent on its structure, morphology and relaxation processes. Furthermore, the properties of composite materials are determined by the characteristics of the polymer matrices themselves, together with reinforcements, and the adhesion of fiber/matrix interface, which mainly depends on the voids and the bonding strength at the interface. A particularly effective approach to surface modification is direct fluorination, as this process does not need any initiation proceeding at practically acceptable rates at ambient temperatures for exothermic nature of this reaction. Besides fluorinated polymers are known to have a set of unique properties, including enhanced mechanical stability and thermaostability and good barrier and membrane properties, which are mainly defined by their surface properties. Here we have focused on the preparation of composites from Kevlar fiber, modified by direct

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fluorination and oxy-fluorination and various thermoplastics such as Ethylene propylene copolymer, syndiotactic polystyrene, and polycarbonate. The effects of such modified Kevlar fiber on the various properties of the aforementioned composites have been studied here. The simulation of fiber orientation in the s-PS matrix has also been studied using mold flow technique under various injection processing conditions.

Firstly thermomechanical behavior of fluorinated and oxy-fluorinated Kevlar fiber-reinforced ethylene propylene (EP) composites has been studied. The composites have been prepared using brabender mixer and are cured using compression molding technique. FTIR study has been performed to understand the chemical reaction occurred due to modification of composites. Thermal behavior and crystallinity of the composites have been studied by DSC, TGA, DMTA and XRD. These studies show that thermal stability, storage modulus, as well as crystallinity of the treated Kevlar fiber-reinforced EP increases in comparison to the untreated derivative because the surface modified Kevlar fiber results in good adhesion between the fiber surface and EP matrix. Tensile strength increases in case of treated Kevlar fiber-reinforced EP in comparison to the untreated one. SEM study supports all the above results. AFM results show that surface roughness increases because of the surface modification resulting from the incorporation of functional group-induced Kevlar fiber.

A comprehensive study on the effect of compatibilizers on the thermal, dynamic mechanical, crystalline and rheological properties of unmodified fluorinated and oxy-fluorinated short Kevlar fiber reinforced ethylene propylene copolymer (EP) has also been carried out under this research work. The compatibilizers used in this study are maleic anhydride grafted Polypropylene (MA-g-PP). The composites were prepared in brabender mixer and were molded in compression molding. The compatibilized samples show improved thermal, dynamic mechanical crystalline as well as rheological properties as a result of better adhesion between the fiber and matrix at the interface. The compatibilizing effect is much more pronounced in case of oxy-fluorinated Kevlar /EP composites in comparison to the untreated and fluorinated Kevlar/EP composites.

The effects of surface modified Kevlar fibers, fiber loading and the resultant crystalline, thermal, dynamic mechanical and morphological properties of Kevlar fiber and thermoplastic ethylene- propylene polymer composites have also been discussed here. Incorporation of surface modified Kevlar fibers enhances the crystallization of the matrix through heterogeneous nucleation compared to unmodified Kevlar fiber. Modified Kevlar fiber reinforcement significantly improved thermal stability of the composites as evidenced by thermo gravimetric analysis. Dynamic mechanical analysis shows that an increase in the storage modulus is more pronounced in case of surface modified Kevlar fibers. The physico-chemical properties also improved with high fiber content in the composites.

Again the effects of the surface modified Kevlar fiber on the crystalline, thermal, dynamic mechanical properties of the Kevlar fiber reinforced syndoitactic polystyrene (s-PS) composites have been explored overhere. The crystallization temperature shifts to a higher value in case of unmodified and fluorinated Kevlar fiber reinforced composites in comparison to the oxy-fluorinated one. Kevlar fibers enhance the crystallization of the matrix through heterogeneous nucleation. Modified Kevlar fiber reinforcement significantly improved the thermal stability of the composites as evidenced by the Thermogrvametric analysis (TGA). Dynamic Mechanical Analysis and Differential Scanning Calorimetry show the shift of T_g to slightly higher value in case of modified Kevlar fiber reinforced s-PS in comparison to

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the unmodified derivative. This is because of the more fiber/matrix interaction in case of modified Kevlar fiber/s-PS. Dynamic mechanical analysis shows that an increase in the storage modulus is more pronounced in case of surface modified Kevlar fibers.

Fluorinated and oxy-fluorinated Kevlar fiber was again blended with SPS at 300⁰C under 10 rpm in a twin-screw extruder. The composites were then injection molded into dumbbell shaped specimens under different conditions like various mold temperatures, injection temperatures, injection speeds. Various physico-chemical characterizations of the composites have been done and effect of all the processing parameters and the chemical modifications were studied. It has been found out that the processibility differ widely with the variation of processing parameters during injection molding. The orientations are different in the skin and core region, which once again affects the flow behavior. The bulk technical properties were found to be the function of the fiber orientations in skin and the core of the injection molded samples. Scanning electron microscopy reveals the better fiber/matrix adhesion in case of modified fiber reinforced syndiotactic polystyrene composites.

Lastly the effect of fluorination and oxy-fluorination of Kevlar fiber on the thermal, dynamic mechanical, crystalline and morphological properties and the simulation of the fiber orientation using mold flow simulation technique under different injection molding parameters of the PC/ LCP/ Kevlar composites have been explored. LCP has enhanced the thermal stability of the PC matrix. Incorporation of modified and unmodified Kevlar fiber further enhances the thermal stability of the concerned composites as evidenced from TGA. XRD study reveals the induction of crystalline behavior of the PC matrix due to the incorporation of the LCP and which is further augmented by the incorporation of the storage modulus of the PC matrix in presence of LCP. Incorporation of unmodified and fluorinated and oxy-fluorinated

Kevlar fiber into the PC/LCP system further enhances the magnitude of storage modulus and this trend is much more pronounced in case of oxy-fluorinated derivative. T_g of the PC phase shifted to the lower temperature side in presence of LCP and it further shifted towards lower temperature side with incorporation of unmodified Kevlar fiber. Incorporation of surface modified Kevlar fiber into the PC/LCP system shifted the glass transition temperature towards higher temperature side as evidenced from DSC and loss peak of the composites. SEM reveals the fine fibrillation of LCP phase in the PC matrix phase in case of oxy-fluorinated Kevlar fiber reinforced derivative indicating the best fiber/matrix adhesion at the interface, although the fibers are covered by the matrix. Mold flow simulation technique reveals that the fiber orientations are different in the skin and core region, which affects the flow behavior. The bulk technical properties were found to be the function of the fiber orientations in skin and the core of the injection molded samples.

Key words: Direct fluorination, Direct oxy-fluorination, Ethylene propylene copolymer, Maleic anhydride grafted polypropylene, Syndiotactic polystyrene, Polycarbonate, Liquid Crystalline Polymers, Thermal stability, Crystallinity, Dynamic Mechanical Properties, Fiber orientation, Adhesion, Mold flow simulation technique.

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Chapter: 1

Introduction



1.1. Introduction:

Polymers play a fabulous role in the art of living of the modern society. The rapid growth of polymer production and use of polymers is one of the most significant trends in the development of the modern world's economy. There are a very few number of branches in industry, transport, households, culture and consumer's goods production, medicine and agriculture, the defense and astronautics where it would be possible to endure with out polymers. Past decade has conceived of a continuous growth in the rate of production and novel application of polymeric materials.

Plastics are unique in many ways. They possess excellent electrical and thermal resistance. Some plastics are as transparent as glass while others are dark and opaque. Many plastics are readily attacked by chemicals and sunlight while some others are highly robust in all most all environments.

Now-a-days most of the plastics are not used in pure form because of the requirements of a specific application and the properties of the same may not match. In order to improve the specific properties and applicability polymers can be modified or custom engineered. One of the main techniques used to improve the properties of the composites of a plastic is its modification by incorporating the modifiers into it. Reinforcements may play a major role as modifiers for enhancing the specific properties. The resulting material is termed as composite.

What is Composite?

Composite is defined as a combination of two or more materials (*i.e. reinforcing elements, fillers and matrix*) differing in form or composition. The constituents keep their own identities: that is, they do not dissolve or merge completely into one another although they act together. Normally, the components can be physically identified and demonstrate an interface between one another. However, because composites are usually utilized for their structural properties, the definition can be restricted to include only those materials, which contain a reinforcement (such as fibers, particles) supported by a binder (matrix) material.

Composites can be divided into two basic forms, composite materials and composite structure. In composite materials the reinforcing materials are surrounded by the continuous matrix on the other hand composite structures are characterized by the discontinuous matrix.

1.2. Types of composites:

The composites can be categorized generally into different types:

1.2.1. Fiber reinforced polymer composites:

Fiber reinforced composites comprise of fibers of high strength, and modulus embedded in a matrix with distinct interfaces between them. In this composite both fiber and matrix retain their physical and chemical identities. In general fibers act as main load bearing constituent, in turn surrounding matrix keeps them intact in their positions and desired orientations (1). Fibrous composites are classified into two broad areas i.e. short fiber reinforced composites and long fiber reinforced composites, which in turn can be categorized into two segments:

> Fiber reinforced thermoset plastics (polyester, epoxy, phenol etc) Fiber reinforced thermoplastic (PPS, PEEK, PEI etc)

1.2.2. Sandwich structures:

FRP facings, aluminum facings, steel facings and foam (PUR, PVC etc.) and/or honeycomb (nomex, carbon, etc.) core's

1.2.3. Fiber metal laminates (ARALL and GLARE):

Fiber metal laminates are new family of hybrid materials consisting of thin metal layers bonded together with the fibers entrenched in an adhesive. They possess the combined properties of both metals and composite materials. 'Arall' variant made up of aramid fibers was first applied on the C-17 military transport aircraft around 1990. Another variant using glass fibers, named 'Glare', was preferred for the Airbus A380 super jumbo in 2001.

1.2.4. Metal Matrix Composites (MMC's):

Metal Matrix Composites are increasingly used in the automotive industry; these materials employ a metal such as aluminium as the matrix, and reinforce it with fibers such as silicon carbide. $\$

1.2.5. Glass matrix composites:

Glass (a relatively inert, inorganic thermoplastic) bestows itself to composite processing methods, which is applicable to polymers such as melt infiltration and compression molding. Glass matrix composites can be developed with high elastic modulus and high tensile strength. It can be maintained up to 600° C and are dimensionally stable because of low thermal expansion of glass matrix in comparison to resin or metal systems. At elevated temperature and high pressure glass matrix composites can be densified. Fabrication procedures of glass matrix composites include dipping graphite or SiC fibers into slurry of glass powder particles in conjunction with a binder. The infused fibers are then collimated to form a tape, dried, placed in a die, heated to remove the binder and then densified with pressure in an inert atmosphere. During application of stress, the high modulus fibers provide the main load-bearing constituent resulting in strengths in excess of those of the parent glass matrix.

1.2.6. Ceramic Matrix Composites (CMC's):

Ceramic Matrix Composites find their applications in very high temperature environments. In CMC's a ceramic acts as the matrix and reinforce it with short fibers, or whiskers such as those made from silicon carbide and boron nitride.

1.2.7. Carbon Carbon Composites:

Carbon Carbon composites are lightweight, high-strength composite materials competent of withstanding temperatures over 3000°C in various environments. Carbon Carbon Composites employ the strength and modulus of carbon fibers to reinforce a carbon matrix to resist the rigors of extreme environments. Aerospace components commonly fabricated from Carbon Carbon include rocket motor nozzle throats and exit cones; nose tips/leading edges and thermal protection systems. Commercial applications of Carbon/Carbon materials include furnace fixturing, heat shields, load plates, heating elements and X-ray targets.

1.3. Constituents of Polymer Composites:

The chief elements of composites include reinforcements and resins (i.e. matrix). Other additives such as catalysts, coupling agents, pigments and adhesives are also added to improve composites properties.

 Reinforcements render stiffness, strength, dimensional stability as well as thermal stability of the composite materials. They encourage effective stress transfer and modify the failure mechanism in composite system. Various factors governing the properties of the composite materials include size, shape, distribution, concentration, and orientation of the reinforcements. Reinforcements are mainly categorized as fibrous, particulate. Fibrous reinforcements are further categorized into two heads: i.e natural synthetic and man made reinforcements. These two types are further classified into various types as described below:

1.3.1. Natural Fibers:

Natural fibers include those made from plant, animal and mineral sources. These natural fibers are widely assorted into the following categories depending upon their sources:

1.3.1.1. Vegetable fibers:

Vegetable fibers are generally constituted primarily of cellulose. Such as cotton, jute, flax, sisal, hemp etc. This fiber can be further categorized into the following:

1.3.1.1.1. Bast fibers:

Bast fibers are termed as the fibers which are collected from the skin or bast surrounding the stem of their respective plant. They are characterised as higher tensile strength than other fibers rendering their applications as durable yarn, fabric, packaging, and paper. Some examples are jute, kenaf, industrial hemp soybean etc.

1.3.1.1.2. Seed fibers:

Fibers collected from seeds or seed cases are termed as seed fibers. Examples are cotton, kapok and coir.

1.3.1.1.3. Leaf Fibers:

Fibers produced from leaves are named as leaf fibers. These fibers run along the length of the leaf such as sisal, caroa, abaca etc.

1.3.1.1.4. Fruit Fibers:

Fibers those are collected from the fruit of the plant are categorised under this section, e.g. coconut (coir) fiber.

1.3.1.1.5. Stalk/ Stem Fibers:

Fibers are actually the stalks or stems of the plant. The examples of such types of fibers are straws of wheat, rice, barley, and other crops including bamboo and grass. The most used natural fibers are cotton, hemp and flax, although sisal, jute, kenaf, and coconut are also widely used.

1.3.1.2. Animal Fibers:

Animal Fibers are generally comprised of proteins; which includes wool, silk, alpaca etc.

1.3.1.2.1. Silk Fiber:

Fiber produced from dried saliva of bugs or similar types of insects during the preparation of cocoons are categorised under this heading. Examples are silk from silk worms.

1.3.1.2.2. Animal Hair (wool or hairs):

Fibers or wool collected from animals or hairy mammals are included in this section. e.g. sheep's wool, goat hair, horse hair, etc.

1.3.1.2.3. Avian fiber:

Fibers collected from birds are named as avian fibers. e.g. feather and feather fiber.

1.3.1.3. Mineral fibers:

Mineral Fibers are naturally occurring fiber or slightly modified fiber procured from minerals. These can be categorized into the following categories:

1.3.1.3.1. Asbestos:

Asbestos are only naturally occuring material fibersThe only naturally occurring mineral fiber. The main variations are chrysolite and amphibloes, crocidolite, tremolite and anthophyllite.

1.3.1.3.2. Ceramic Fibers:

Glass fibers (Glass wool, Quartz), silicon carbide, aluminium oxide and boron carbide

1.3.1.3.3. Metal Fibers:

Aluminum fibers are categorised under this heading.

1.3.2 Man-made fibers:

The man-made fibers are classified into two different categories (regenerated and synthetic) depending on the method in which they are manufactured (2).

1.3.2.1. Regenerated fibers:

Regenerated fibers are made from natural materials by processing these materials to form a fiber structure. Also called cellulosics, regenerated fibers are derived from the cellulose in cotton and wood pulp. Rayon and acetate are two common regenerated fibers.

Rayon is manufactured by fibers composed of regenerated cellulose in which different substituents have replaced not more than 15% of hydrogen of the hydroxyl groups (1)

1.3.2.2. Synthetic Fibers:

Synthetic fibers are made entirely from chemicals. Synthetic fibers are usually stronger than either natural or regenerated fibers. Synthetic fibers and the regenerated acetate fiber are thermoplastic; they are softened by heat. Therefore manufacturers can shape these fibers at high temperatures, adding such features as pleats and creases. Synthetic fibers will melt if touched with too hot an iron. The most widely used kinds of synthetic fibers are nylon (polyamide), polyester, acrylic, and olefin.

1.3.2.2.1: Nylon:

Nylon is a thermoplastic material, first used commercially in a nylonbristled toothbrush (1938), followed more famously by women's "nylons" stockings (1940). It is made of repeating units linked by peptide bonds (another name for amide bonds) and is frequently referred to as polyamide (PA). Nylon was the first commercially successful polymer and the first synthetic fiber to be made entirely from coal, water and air.

1.3.2.2.2: Kevlar:

Kevlar is DuPont trade name of poly(p-phynelene terephthalamide) and was first created in DuPont's labs in 1965 by Stephanie Kwolek and Herbert Blades (3), Kevlar was first used commercially in the early 1970s. It can be spun into ropes or sheets of fabric that can either be used as-is, or used in the construction of composite components. Kevlar is now used in a wide range of applications, from bicycles to body armor, due to its high strength-to-weight ratio, and it is 5 times stronger than steel on an equal weight basis (3). Under water, Kevlar has less of an effect to ballistic projectiles, although it does have water resistant properties (4). It is a member of the Aramid family of synthetic fibres and a competitor of Twaron manufactured by Teijin.

1.3.2.2.3: Glass fibers:

Glass fibers are the most common of all the reinforcing agents for polymeric matrix composites (2). Glass Fiber is used for: industrial, automotive, and home insulation (Fiberglass) reinforcement of composite and plastics specialty papers in battery separators and filtration

1.3.2.2.4: Metallic Fibers:

Metallic fiber (1946) is used for: adding metallic properties to clothing for the purpose of fashion (usually made with composite plastic and metal foils) elimination and prevention of static charge build-up conducting electricity to transmit information conduction of heat

Table1.1: Properties of Kevlar and other competeitive materials:

Properties	Nylon	Kevlar	Kevlar	E-	Steel
	66	29	49	Glass	
Specific gravity	1.14	1.44	1.45	2.55	7.86
Tensile Strength (kNm ⁻²)	1000	2750	2760	1700	1960
Tensile modulus (MNm ⁻²)	5.52	82.7	131	68.9	200
Elongation at break (%)	18	5.2	2.4	3.0	2.4

Source: Ref. 5

For several applications fibers should prepared and modified with respect to:

- Homogenization of the properties of the fibers
- Degree of of elementarization and degumming
- Degree of polymerization and crystallization
- Good adhesion between the fibers and matrix
- Moisture repellence
- Flame retardant properties

1.3.3. Matrices:

Another major constituents of the fiber reinforced composites is the matrix. Matrix should be categorized under two heads: thermoplastic and thermosetting.

The key difference between thermoplastics and more traditional thermoset based polymers composites belongs to the behaviour of matrix during processing. The thermoplastic matrix needs not undergo a cure process to achieve its final mechanical, trhermal as crystalline properties; all that required is melting, shaping and subssequent solidification. The range of conventional thermoplastic composites and their resultant properties mainly depend on the average length of the fibers during molding.

The most important among common polymeric matrices are polyester and epoxy resins.Cured epoxy resins constitute prime matrix for high performane glass, aramid and carbon fiber composites (6, 7) whereas the unsaturated polyester resins are primarily used in industrial applications. The advantages of the former include their resistance to water, a variety of chemicals, weathering and aging. Polyimides represent the largest class of high temperature polymer matrices used in polymer composites today (8, 9) and have service temperatures in the range 250-300^oC and are availabe both as thermoplastics and or as thermosets.

Thermosetting resins are crosslinked with peroxide to obtain high modulus, strength and creep resistance. However, they exhibit extreme brittleness. Thermoplastic resins are easier to fabricate than thermosetting resins (10). Besides, they can be recycled also.

Ethylene polypropylene copolymers are thermoplastic polymers consisting better resistance to stress cracking than polyethylene and polypropylene. EP is easily available, economic and well established and successfully used as effective matrix for fiber reinforced polymer composites. The most intriguing properties of s-PS are high melt temperature (about 270 0C), high crystallinity and rapid crystallization rate. Thus, s-PS exhibits not only good chemical resistance but also enhanced mechanical performance at elevated temperatures as well [11-13]. However, s-PS is poor in impact resistance and therefore, it has suffered the disadvantage that it is inevitably limited in the scope of application as a construction material [14].Polycarbonate is becoming more common in house wares as well as laboratories and in industry, especially in applications where any of its main features—high impact resistance, temperature resistance, and optical properties—are required.

The typical properties of EP, s-PS and PC are listed in Table 1.2:

Properties	Etylene	Sydiotactic	Polycarbonate
	propylene	polystyrene	
Density (g/cm ³)	0.9	1.02	1.2-1.22
Tensile strength (MPa)	26	45	55-75
Elongation at break (%)	500	30	80-150
Melting temperature (⁰ C)	165-200	270-290	267

 Table 1.2: Representative properties of some polymeric materials:

1.4. Interface:

The structure and properties of the fiber/matrix interface offers significant role in governing the mechanical and physical properties of the fiber reinforced composites. In fiber reinforced thermoplastics, surface of the fiber side, surface of the matrix and the phase between fiber and matrix are collectively called as interface (15).

The large difference between the properties of the fibers and the matrix are communicated through the interface or in other words the stress acting on the matrix polymer is being transferred to the fibers (the main load bearing constituents) through the interface. These interface effects are ascertained as a type of adhesion phenomenon and are often interpreted in terms of the surface structure of the bonded materials, i.e. surface factors such as wettability, surface free energy, the presence of the polar groups on the surface and surface roughness of the material to be bonded.

A number of assumptions have to be made about the properties of the interface for the theoretical analysis of stress transfer from fiber to the matrix as given below:

- The matrix and the fibers behave as classic materials.
- The interfacial bond is infinitesimally tenuous.
- The bond between the fiber and the matrix is perfect.
- The fibers are arranged in a regular or repeating array.
- The materials close to the fiber has the same properties as material in bulk form.

Some mathematical models are necessary to correlate these assumptions in polymeric materials. Figure 1.1 shows the fracture surfaces of fiber reinforced composite with different mode of interface.



Fgiure 1.1: Diagrams of typical frature surface of unudirectional composite loaded in tension along the fiber direction a) composite with strong interfacial bond, d) composite with intermediate interfacial bond, c) composite with poor interfacial bond.

1.5. Composite fabrication technique:

Fabrication techniques involve the conversion of material from a less useful shape to a more useful one. The choice of fabrication technique of fiber reinforced composites solely depends on the performance, economics and application of the materials. It is also related to a number of factors such as number of molded surface, components required, item complexity and type of reinforcements. Fabrication methods in the composites are divided into following categories:

- Hand lay up
- Vacuum bag molding
- Filament winding
- Centrifugal casting
- Compression molding
- Pultrusion
- Resin transfer molding
- Injection molding

An ideal processing technique is characterized by the following aspects (16):

- High productivity
- Minimum material cost
- Maximum geometrical flexibility
- Maximum property flexibility
- Minimum finishing requirement
- Reliable and quality manufacture

Compression molding is the fabrication technique in which the molding material (generally preheated) is first placed in an open, heated mold cavity. In this technique the mold remains closed with a top force or plug member. Pressure is applied to force the material into contact with all mold areas, and heat and pressure are maintained until the molding material has cured. The process employs thermosetting resins in a partially cured stage, either in the form of granules, putty-like masses, or preforms. Compression molding is a high-volume, high-pressure method suitable for molding complex, highstrength fiberglass reinforcements and aromatic fiber reinforcements (17). Advanced composite thermoplastics can also be compression molded with unidirectional tapes, woven fabrics, randomly orientated fiber mat or chopped strand. The advantage of compression molding is its ability to mold large, fairly intricate parts. Compression molding results fewer knit lines and less fiber-length degradation than injection molding.

Injection molding is a manufacturing technique for making parts from thermoplastic material in production. In this technique molten plastic is injected at high pressure into a mold, which is the inverse of the product's shape. After a product is designed by an Industrial Designer or an Engineer, molds are made by a moldmaker (or toolmaker) from metal, usually either steel or aluminum, and precision-machined to form the features of the desired part. Injection molding is widely used for manufacturing a variety of parts, from the smallest component to entire body panels of cars. Injection molding is the most common method of production, with some commonly made items including bottle caps and outdoor furniture. The most commonly used thermoplastic materials are polystyrene (low cost, lacking the strength and longevity of other materials), ABS or acrylonitrile butadiene styrene (a co-polymer or mixture of compounds used for everything from Lego parts to electronics housings), nylon (chemically resistant, heat resistant, tough and flexible - used for combs), polypropylene (tough and flexible - used for containers), polyethylene, and polyvinyl chloride or PVC (more common in extrusions as used for pipes,
window frames, or as the insulation on wiring where it is rendered flexible by the inclusion of a high proportion of plasticiser).

Injection molding can also be used to manufacture parts from aluminum or brass. The melting points of these metals are much higher than those of plastics; this makes for substantially shorter mold lifetimes despite the use of specialized steels. Nonetheless, the costs compare quite favorably to sand casting, particularly for smaller parts.

1.6. Factors influencing the composite properties:

1.6.1. Strength, modulus and chemical stability of the fiber and the polymer matrix:

The mechanical properties of fiber-reinforced composites are widely regulated by the strength and modulus of the reinforcements (18). As it is mentioned earlier that in fiber reinforced composites fibers are the main load bearing constituents while the matrix keeps those fiber in their desired positions and orientations. Matrix should be chosen as per the requirements of the end product. There are many other factors such as cost, ease of fabrication and environmental conditions (e.g. temperature, humidity) in which the end product is going to be used should also be considered. The weathering and chemical resistance of the matrix, design stresses and the required durability of the end product are also deserve supreme importance in regulating the composite properties. The main role of the matrix in a fiber-reinforced composite will alter depending on how the composite is stressed (18). In case of compressing loading, the matrix must prevent the fibers from buckling, and thus offers a very critical part of the composite. If this fact is ignored then the reinforcing fibers could not carry any load. On the other hand, a bundle of continuous fibers could sustain high tensile loads in the direction of filaments with out a matrix. The matrix also provides a transfer medium so that even if a single fiber breaks, it does not lose its load carrying capacity.

1.6.2. Influence of fiber orientation and volume fraction:

Fiber orientation and volume fraction have significant role on the mechanical as well as other properties of the fiber reinforced polymer composites (1). With respect to fiber orientation, two extreme cases are possible-parallel alignment of the longitudinal axis of the fibers in a single direction and totally random orientation. These two extremes are depicted in Figure 1.2a and 1.2b respectively. Normally continuous fibers are aligned and discontinuous ones are randomly oriented. Longitudinally aligned fiber reinforced composites exhibit inherent anisotropic thermal, mechanical and dynamic properties, where the maximum strength and reinforcements are achieved along the direction of fiber orientation (1). On the other hand, transversely orientated fiber reinforcements are virtually non existent, fracture usually occurs at very low tensile stress, which may be even less that the pure matrix. In randomly oriented fibrous composites, strength lies between these two extremes. Hence, the prediction of fiber orientation in the fiber reinforced composites is very much important in order to derive the properties of the same.



Figure 1.2: Schematic representation of a) continuous and aligned and b) discontinuous and randomly oriented fiber reinforced composites

1.6.2.1. Fiber orientation in injection molded fiber reinforced composites:

In injection molding the fibers are considered to be suspended in the matrix and thereby orient themselves in response to the kinematics of the flow, mold cavity and other neighboring fibers. However, fiber suspensions often demonstrate an anisotropic behavior due to a flow-induced fiber-alignment in the flow direction. The properties of short-fiber-reinforced thermoplastic composites, however, suffers from a problem associated with fiber orientation,

which in turn depends on the **processing conditions** and the geometrical shape of the mold such as gating, inserts, and section thickness [19–25]. During the filling of an injection molding die, three flow regions normally exist.

These regions are:

- a three dimensional region near the gate
- a lubrication region: where no significant velocities out of the main flow plane exist and where the majority of the flow is contained
- • a fountain flow region at the flow front



Figure 1.3: Flow regions during the injection molding process

The effect of flow behavior on fiber orientation is complex but two rules of thumb have been demonstrated:

- Shearing flows tend to align fibers in the direction of flow.
- Stretching flows tend to align fibers in the direction of stretching. For a center gated disk, the stretching axis is perpendicular to the radial flow direction as can be seen from the Figure 1.4.



Figure 1.4: the representative scheme of alignment of fibers

The orientation of fibers in an injection molded parts consists of three different layers:

- a core created by in-plane fiber motion during mold filling
- shell layers on either side of the core, with a flow aligned orientation caused by gapwise shearing
- skin layers at the mold surface

This difference in fiber orientation in different region affects the mechanical and thermal properties of the molded fiber reinforced composite

parts (26). Hence it is of worth interest to predict the fiber orientation under different processing conditions. There are many reports available which demonstrates the numerical/ analytical (27-28) as well as computer aided simulation approach (29) to evaluate the fiber orientation in injection molded short fiber reinforced composites under different molding conditions. Zhou et al (30) reported the behavior of fiber orientation probability distribution function in the planar flows. In their research work they have reported about the effect of fiber orientation on the planar flow behavior of the short fiber reinforced composites. Chung et al (31-32) reported the polymer melt flow and weld line strength of injection moldings made by using the co injection molding technique. A comprehensive study on the effect of processing variables on microstructure of injection molded short fiber reinforced polypropylene composites have been reported by Singh et al (22). S.S.S. Imihezri et al (33) investigated mould flow and component design analysis of polymeric based composite automotive clutch pedals. Patcharaphun et al (34) have reported the properties enhancement of short glass fiber-reinforced thermoplastics via sandwich injection molding. Although many research works have been reported leading to the theoretical or numerical approach for the prediction of fiber orientation, there are still a large scope remains for the computer aided simulation of the fiber orientation.

1.6.2.2. Theoretical basis for fiber orientation prediction:

Motion of a single rigid ellipsoidal particle immersed in a viscous Newtonian liquid was considered by Jeffery (35). Evolution equation for a single rigid ellipsoidal particle was developed, and it is the base of almost all the fiber orientation constitutive modeling.

Fiber suspensions are characterized in terms of the number of fibers per unit volume n, fiber length L and diameter D as dilute $(nL^3 \le 1)$, semi-dilute $(nL^3 \gg 1, nL^2D \ll 1)$ and concentrated $(nL^3 \gg 1, nL^2D \gg 1)$ regime. nL^3 means the number of interacting fibers in a volume swept by a single fiber and nL^2D means an excluded volume of interacting fibers due to a line approximation of a fiber. Currently, many researchers have developed many numerical simulation programs with different methods for the description of fiber orientation including multiple fiber-fiber interaction. However, some of those simulation programmes using direct calculation of fiber motion (36-39) require incredible computation time which is the reason why such a numerical simulation method cannot be accommodated. Calculation of fiber orientation state using the probability distribution function (DFC) is one of them. Instead, a tensor representation of orientation state (40), which is a pre-averaging concept of DFC, is widely used for its efficiency, compactness and above all, manageable computation time. However, it is necessary to introduce a closure approximation to express the higher order tensor in terms of lower order tensors for a closed set of equation since the evolution equation for orientation tensor involves the next higher even order tensor.

The second order orientation tensor a_{ij} provides an efficient description of fiber orientation in injection moldings. The predicted fiber orientation, which is a probability distribution in 3D space, can be represented by the following equation, and graphically as the ellipsoid in figure 1.5.

$$\mathbf{a}_{ij=} \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \rightarrow \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}; (e_1 \ e_2 \ e_3)$$



Figure 1.5: Orientation ellipsoid defined by general 2nd order orientation tensor

Thus the tensor has nine components, with the suffixes for the tensor terms being:

1) in the flow direction, 2) transverse to the flow direction and 3) in the thickness direction.

The X-Y (or 1-2) axes are applied to flow plane and the Z-axis in the thickness direction i.e. out of the 1-2 flow plane. Due to tensor symmetry

 $a_{ij}=a_{ji}$, and a normalization condition $(a_{11}+a_{22}+a_{33}) = 1$, the original nine components reduce to five independent components. These three major orientation components have been included in the orientation considerations: a_{11} represents the fiber orientation in the flow direction, varying from 0 to 1.0 a_{22} represents the fiber orientation transverse to the flow, varying from 1 to 1.0 a_{13} is the tilt of the fiber orientation in the 1-3 plane, varying from -0.5 to 0.5. However, the flow direction orientation (a_{11}) term possesses most of the quantitative information about microstructure and is most sensitive to flow, processing and material changes. In modern concept the tensor components in Synergy are named with a "T" rather than an "a", and show the specific axis names, x, y and z, rather than the generic axis names 1, 2 and 3.

For semi concentrated suspension, Dinh and Armstrong proposed a model for prediction of fiber orientation (41). In their proposed model the fiber orientation follows the bulk deformation of the fluid with the exception that the particle cannot stretch.

Whereas for concentrated suspensions a term, called "the interaction coefficient" (or C_I), has been incorporated in Folgar and Tucker (42) model of fiber orientation, where interactions among fibers tend to randomize the orientation and the term takes the same form as a diffusion term and since interactions only occur when the suspension is deforming, the effective diffusivity is proportional to the strain rate finally the dimensionless C_I term determines the strength of the diffusion term. The model is represented as given below:

where $\alpha = 3$ for 3D and 2 for 2D (planar) orientation, v_k = velocity component, ω_{ij} = velocity tensor, γ_{ij} = deformation tensor, λ = constant depending on the geometry of the particle, δ_{ij} = unit tensor, C_I= interaction coefficient.

As mentioned earlier that introduction of closure approximation is very much necessary to express the tensor in terms of lower order tensors for a closed set of equation because of the evolution equation for orientation tensor involves the next higher even order tensor. But closure approximation is too much challenging as it produces error in prediction of fiber orientation. In order to minimize these effects some proposal also been proposed in the Advani Tucker fiber orientation model- introduction of more accurate closure, introduction of a new orientation model that considers the closure error. The effect of the closure approximation is to predict too much out-of-plane orientation. This result has been addressed by the fiber orientation model form proposed by Moldflow.

1.6.2.3. Moldflow's fiber orientation model:

In mold flow technique, the simulation of the orientation of fibers can be done using Jeffery's model (35) in conjunction with Tucker-Folgar term (42).

Moldflow model considers two assumptions:

 the Tucker-Folgar model gives acceptable accuracy for the prediction of fiber orientation in concentrated suspensions

Hybrid closure is used as it's form is simple and has good dynamic behavior

Into moldflow orientation model an extra term called "thickness moment of interaction coefficient (D_Z) " has been introduced.

In moldflow model while putting $C_I = 0.0$, the model takes the form of Jeffery's (35) model, the magnitude of D_Z regulates the significance of the randomizing effect in the out of plane direction due to the fiber interaction, and when $D_Z = 1.0$, then this model gives the Folgar-Tucker orientation model.

However, for injection molding situation, the flow hydrodynamics cause the fibers lie mainly in the flow plane. Their ability to flow out-of-plane is severely less. This mechanism predicts that the randomizing effect of fiber orientation is much smaller out-of-plane than in the in-plane directions, hence a small D_Z value. Thus decreasing D_Z parameter out-of-plane orientation can be diminished and on the other hand thickness of the core layer can be increased. The simulation treats this problem as being symmetric about the mid plane.

1.6.3. Volume Fraction:

Fiber volume fraction plays a major role in predicting the properties of the fiber reinforced composites, especially hybrid composites. Fiber volume fraction is represented in equation given below:

 $V_f = V_f / V_c$ (for normal composites)..... 1.2

 $V_f = V_F/V_C$ (for hybrid composites).....1.3

Where V_f = volume fraction of fiber, V_c = total volume of composites, V_F = V_{f1} + V_{f2} . V_F is the total volume fraction of two types of fibers. Matrix volume fraction is given by the following equation:

$$V_{m} = V_{m} / V_{c} \dots 1.4$$

Where V_m = the volume fraction of the matrix.

For a fiber reinforced composite an optimum spacing must be maintained to achieve the maximum properties, which is the minimum allowable spacing between the fibers, below which the structure will start to disintegrate under loading before the tensile failure. This minimum spacing is defined as the maximum volume fraction allowable for a composite.

1.6.4. Influence of fiber length:

The strength of fiber reinforced composites not only depends on the tensile strength but also on the extent to which an applied stress is transmitted to the fibers from matrix (1, 5). The extent of this load transmittance is a function of fiber length and the strength of fiber-matrix interfacial bonds. Under an applied stress, this fiber-matrix bond ceases at the fiber ends resulting a matrix deformation. There is no stress transfer from the matrix at the fiber extremity. Hence a critical fiber length giving rise to critical aspect ratio, length to diameter ratio (l/d) should be maintained to effective stress transfer between the fiber and matrix at the interface.

1.6.5. Influence of voids:

During the incorporation of fibers in to the matrix or during the manufacture of laminates, air or other volatiles are trapped in the material (18, 43). The trapped air or volatiles exists in the cure laminate as microvoids,

which may significantly affect some of its mechanical properties. Paul and Thomson (44) and Bascom (45) have investigated the origin of voids and described the various types of voids encountered in the composite and the means to reduce the void content. The most common cause of voids is the incapability of matrix to displace all the air which is entrained with in the roving or yarn as it passes through the resin impregnator. The rate at which the reinforcements pass through the matrix, the viscosity of the resin, the wettability or contact angle between the matrix and the fiber surface and the mechanical working of the fibers, etc. will affect the removal of the entrapped air. A high void content (over 20%) usually leads to lower fatigue resistance, greater susceptibility to water diffusion, and increased variation (scatter) in mechanical properties.

1.6.6. Influence of coupling agents:

Incorporation of coupling agents into the fiber reinforced composites offers optimum physical properties of the same and retains these properties of the composites after environmental exposure. Good bonding at the interface can be achieved by modifying the interface with various coupling agents.

An important technique for improving compatibility and dispesibility between the filler and the matrix is to develop a hydrophobic coating of a compatible polymer on the surface of the filler prior to mixing with the polymer matrix. Generally, coupling agents facilitate better adhesion between the filler and the matrix. The selection of coupling agents which can provide both strength and toughness to a considerable degree is important for a composite material.

1.7. Surface modification:

Surface modification of both matrix/ or fiber is a key area of research at present to achieve optimum fiber/ matrix properties.

1.7.1. Surface modification of Fibers:

Reinforcing fibers can be modified by physical as well as chemical methods.

i) Physical methods of modification:

Physical treatments alter the structural and surface properties of the fibers thereby influence the mechanical bonding in matrix-fiber interface. These physical treatments include electric discharge method using corona or cold plasma. In the case of cold plasma treatment, depending on the type and nature of the gas used, a variety of surface modifications like crosslink could be introduced. In this process surface free energy could be increased or decreased and reactive free radicals onto the fiber surface could be produced (46). For Kevlar fiber where moisture absorption is known to have deteriorating effects, the plasma process is inherently an effective drying process providing further benefits (47). Corona treatment is one of the most interesting techniques for surface oxidation activation. This process changes the surface free energy of the fibers (48).

ii) Chemical methods of modification:

Chemical methods offer more convenient techniques to modify the fiber surface (49-51). Chemical methods bring about the compatibility between

the two polymeric materials either crating some functional groups on the fiber surface by means of chemical reactions or introducing a third material into the composites that has properties in between those other two.

Park et al. reported the chemical treatment of Kevlar surface by Phosphoric acid significantly affected the degree of adhesion at interfaces between Kevlar fibers and epoxy resin matrix (51). Yue et al. (52) improved the interfacial shear strength of Kevlar fiber/epoxy composites significantly, through chemical treatment of the fiber with organic solvents. Wu et. al (53) have proposed acid treatments as the modification tool for PBO, Kevlar and Carbon fiber. they have noticed a remarkable change in the surface free energy of those modified fibers. Mavrich et.al (54) have demonstrated the infra red mapping of epoxy reacted Kevlar/Epoxy system.

Different types of coupling agents are used to modify the fiber surface in order to enhance the fiber surface functionalities. Silanes have been the most frequently used coupling agents (55). Silanes provide dual functionalities in one molecule, so that one part of the molecule forms a bond to the fiber surface while other part forms a bridge with the matrix molecule. Ai et.al (56), have used alkoxysilane as an effective coupling agent for kevlar fiber in kevlar/epoxy system. They have reported that with surface modification the adhesion between the fiber and the matrix increases resulting to the enhancement of iinterlaminar shear strength. Andreopoulos (57) have used acetic acid anhydride, sulfuric acid-acrylamide, and methacryloyl chloride as coupling agents to introduce the polar functional groups onto the Kevlar surface and among them methacryloyl chloride appeared to be the most effective coupling agents for Kevlar fiber. Menon et.al (58) have reported the effectiveness of the titanate coupling agents in Kevlar/phenolic composites. They have demonstrated an improved moisture resistant and flexural strength for modified systems. Copolymers can also be used as effective coupling agents for fibrous systems. MA-g-PP and MA-g-PE provide covalent bonds across the interface Polypropylene-cellulose systems.

1.7.2. Surface modification of matrix polymers:

The wettability of the matrix polymer on the fiber surface depends on the viscosity of the matrix and the surface tension of both materials. For better wetting of the matrix on the fiber surface, surface tension of the matrix should be as low as possible, it should be at least lower than the reinforcing fiber materials. Hence the modification of matrix in a fiber reinforced composites consist of the following methods:

a) Chemical treatments:

The polymer surface can be modified by introducing polar groups onto the matrix surface. When a polymer is treated with highly oxidative chemicals such as chromic anhydride/tetracholoroethane, chromic acid/acetic acid, chromic acid/sulfuric acid under suitable conditions, polar groups are introduced on the polymer surface and the surface characteristics are improved (59, 60).

i) Coupling agents for olefinic matrixes:

The surface of the polyolefines can be activated by treating it with the chemicals through the formation of polar groups such as >C=O, -OH, -COOH

and –SO₃H. Rasmussen et al determined these polar groups (61) qualitatively in detail.

In recent years so many coupling agents are being available in case of polyolefin matrix. Souza et al (62) have reported the effectiveness of ethylene propylene-diene-compolymer (EPDM), ethylene-vinyl-acetate-copolymer (EVA), and styrene-ethylene/butylene-styrene triblock- copolymer (SEBS) as PP/HDPE blends. Reichertet et compatibilizers in al (63) have demonstrated the compatibilizing effect of MA-g-PP in PP / organoclay nano composites. Laredo et al (64) has reported the effect of compatibilization of MA-g-PP on the dynamic properties of PP/nylon 6 blends. R. Krache et al (65) studied the effect of compatibilization of polystyrene–poly (ethylene butylene)-polystyrene copolymer (SEBS) and SEBS-grafted maleic anhydride (SEBS-g-MAH), on the morphology and rheology of the binary and ternary blends of polyethylene, polypropylene and polyamide 6, 6. Kim et al (66) have reported the compatibilization effect of MA-g-PP on the morphological, rheological, thermal, dynamic mechanical and mechanical properties of the EPDM and Nylon 6 blends. Annerfeldt et al (67) have studied the influence of hyperbranched polymer grafted polypropylene (PP-HBP) on the morphology of polypropylene (PP) /polyamide 6 (PA6) blends. Jiang et al (68) have demonstrated the effect of MA-g-PP as compatibilizer on the rhological, crystalline, morphological as well as mechanical properties of Dynamically Cured Polypropylene/Epoxy Blends. Manchado et al (69) studied the effect of MA-g-PP on the rheological, mechanical, crystalline properties

and interfacial adhesion of PP/EPDM/Flax Fiber Composites. Arroyo et al (70) have reported the effect of EPDM on the morphology/behavior relationships and recyclability of PP/EPDM and aramid fibers.

ii) Coupling agents for styrenic matrices:

The most intriguing properties of s-PS are high melt temperature (about 270 ^oC), high crystallinity and rapid crystallization rate. Thus, s-PS exhibits not only good chemical resistance but also enhanced mechanical performance at elevated temperatures as well [71-73]. However, s-PS is poor in impact resistance and tear resistance and therefore, it has suffered the disadvantage that it is inevitably limited in the scope of application as a construction material [74]. Recently to improve the processability and the physical properties of s-PS many procedures are being followed. Various modification processes involve the preparation of functionalized s-PS, such as sulfonated s-PS [75], acetylated s-PS [76], maleic anhydride grafted s-PS [77], and hydroxylated s-PS [78]. In addition, polymer blends also provide a method for s-PS modification, for example, blending a rubbery elastomer and/or other thermoplastic resin with s-PS may broaden the commercial utility of s-PS [79–81].

iii) Coupling agents for polycarbonate matrices:

Chiang et al (82) studied the effectiveness of three kinds of compatibilizers, methacrylate-butadiene-styrene (MBS), ethylene-vinyl acetate (EVA), and styrene-maleic anhydride (SMA) on the flame retardant behavior as well as crystalline and morphological properties of the polycarbonate (PC)/acrylonitrile-butadiene-styrene (ABS) alloy. Tjong et al (83)

demonstrated the effect of reactive compatibilizers on the mechanical properties of polycarbonate/poly(acrylonitrile-butadiene- styrene) blends using MA-g-PP and solid epoxy resin (bisphenol type-A). Kim et al (84) studied the compatibilizing effect of two types of poly(allyl-co-maleic anhydride) on the morphological, dynamic mechanical and thermal properties of polycarbonate/nylon alloy.

b) Physical methods:

Physical method includes UV irradiation, corona discharge treatment and plasma treatment.

1.8. Fluorination and oxy-fluorination as polymer surface modification tool:

Direct fluorination and oxy-fluorination plays a tremendous role as a surface modification technique for polymeric materials as it possess various advantages as given below:

1) The elemental gas is used to modify polymeric materials. Due to very highenergy release during the main elemental stages, the fluorination occurs at room temperature or below [85-87]. The process does not need any initiation or catalyst.

2) Gaseous mixtures of fluorine, oxygen, nitrogen, helium, chlorine, and chlorine mono-fluoride may be used for direct fluorination.

3) The reaction proceeds by the diffusion limited process.

4) The fluorine treated plastics consists of totally fluorinated, untreated virgin layer separated by a thin transition layer.

5) The thickness of the modified layer polymer can be put under control over $\sim 0.01-10 \mu m$ range.

6) This technology is so called "dry" one (only gases are used) and polymeric article of any shape can be modified.

7) One of the main advantages of direct fluorination and oxy-fluorination is that the only thin surface layer of polymer is modified and hence the bulk properties of the polymer are not practically changed.

Fluorination and oxy-fluorination offers improved properties in comparison to the unmodified polymeric materials as listed below:

1) Barrier properties:

In recent times one of the most commercially important applications of the direct fluorination and oxy-fluorination of polymeric materials is the enhancement of barrier properties (85). Direct fluorination creates the barrier to permeation of hydrocarbons due to several reasons: firstly fluorination causes significant increase of the specific gravity (88-94) as a result free volume decreases. 2ndly direct fluorination results in the cross linking of polymers (85, 90, 92, 93, 95-97) hence swelling and plasticization effects under the action of hydrocarbons are suppressed. This cross linking also results in the decrease of the permeability. Finally the surface energy of fluorine treated polymer surfaces in many cases is increased and hence the solubility of low polar organic liquids in fluorinated polymers is decreased.

This enhanced barrier properties of fluorinated polymers can be employed in the industrial applications. Direct fluorination of polymer containers for packaging of industrial and consumer chemicals decreases the loss of liquids which are stored inside the container. Carstens (98, 99) has shown that the loss of chemicals such as alachlor, bromoxynil, chlorpyrifos, creosote, paints, polishes, hand cleaners etc from HDPE containers can be reduced by a factor one or two orders of magnitude. Leakage of toluene from HDPE containers also can be reduced by a factor 100 (100), 50-60 (101), 15 (102) and pentene by a factor 100 (103). Direct fluorination also improves the barrier properties of natural and synthetic fibers (104), polyurethane (105), LLDPE, PP, PET (98, 99). Direct oxy-fluorination also enhances the barrier properties in some cases (87, 106, 103).

ii) Membrane technology:

Direct fluorination and oxy-fluorination results a significant decrease of the gas permeability of multiatomic gases (CH₄, C₂H₄) as compared to light ones hence offers an important role in membrane technology. A large contribution to the modification of gas separation properties of polysulfone (PSF), asymmetric membranes and films, polyvinyl trimethyl silane (PVTMS) membranes and films, Poly(phynelene oxide) (PPO) composite membranes by direct fluorination have been investigated by Mohr et al (106-107) and Leroux et al (108-110). The direct fluorination can be used to modify polymer films used for food storage and preservation. Initially permeability of oxygen can be highly decreased under fluorination of polymers. Kharitonov et al have shown that oxy-fluorination enhances the effect of permeability reduction in an appreciable amount (88, 90, 92-94, 111). As direct fluorination and oxyfluorination vary the selectivity of separation of gas mixtures the fluorination and oxy-fluorination can be used to modify the polymer packaging for food storage such as modified atmosphere packaging, controlled-atmosphere packaging and equilibrium-modified atmosphere (98-99).

iii) Adhesion properties:

The most appealing and important properties of fluorinated and oxyfluorinated polymers are the enhanced adhesion in comparison to the unmodified polymers. This improved adhesion is attributed to the incorporation of surface functionalities arises due to the following reasons:

i) The partial substitution of fluorine for hydrogen, cross linking (formation of C-C bonds) destruction of C-C bonds can take place (112).

ii) Free radical initiated chain scission or rearrangements.

iii) Direct oxygenerates $-C \not\in_{F}^{O}$ $-C \not\in_{H}^{O}$ additional

>C=O, -C groups can be inserted into the polymer structure. Oxy-fluorination is accompanied with the graft polymerization. It is well known that in oxy-fluorinated polymeric materials surface a controlled amount of long living peroxy radicals (RO_2^*) are generated (88-92). This method is the most prospective one because the surface properties of the modified polymers will be determined by the grafted polymer and there is much more possibilities to

vary the surface properties-e.g. from hydrophobic to hydrophilic ones. Moreover, the grafted polymer can also be further fluorinated and oxyfluorinated.

The interactions of the functionalized polymer surface (fibers or fillers) and the adhesive or matrix material may be expressed in terms of i) improved wetting, ii) polar-polar interactions, iii) dispersive interactions promoted by the incorporation of polarizable groups such as carbonyl and iv) the formation of covalent bonds. The role of surface functionalities may also be explained by the general theory of surface acid-base interactions proposed by Fowkes (113).

The direct fluorination and Oxy-fluorination have already shown to improve adhesion of polyolefines (HDPE) (98, 99, 114-116), LDPE (115), ethylene- vinyl- acetate copolymers (117), rubber (118), PP (98, 99, 119), polymers of aliphatic mono-1-olefines and elastomeric, resinous polymers of conjugated dienes and vinyl-substituted aromatic compounds (120), poly (arylene sulfide) (121), polyamides and polyethers (122), butadiene-styrene copolymer (116), and other polymers (123). Wettability, hydrophilicity and hydrphobicity of polymers also can be modified (122, 124-125). The review of the influence of fluorination and oxy-fluorination on the adhesion and surface energy can be found in (87). The possible commercial applications of the adhesion improvement of the paint receptivity of polymer goods, reinforcement of the polymer composites, increased resistance to delamination in coated flexible films etc (87, 88, 89). Equipment to improve adhesion of polymers by the direct fluorination and oxy-fluorination is described in (85, 126).

1.9. Synthetic fiber reinforced composites:

Fiber reinforced plastics (FRP) have been widely accepted as materials for structural and non-structural applications in recent years. The main reasons for the increased interest in FRP for structural applications, are high specific modulus, high strength of the reinforcing fibers. Various synthetic and natural fibers are being used as the reinforcing agents in FRP. Among natural fibers jute (127), sisal (128), henequen (129) fibers are used as successful reinforcements. Although natural fibers are inexpensive, easily available, biodegradable, they are not environmentally stable, chemically inert along with hydrophilic in nature and of low strength.

Synthetic fibers are high-performance fibers possessing very high levels of at least one of the following properties: tensile strength, operating temperature, heat resistance, flame retardancy and chemical resistance (130). The resistance to heat and flame is one of the main properties of interest for determining the working conditions of the fibers (131).

Short fiber reinforced thermoplastic-based polymer composites have drawn the attention of many engineering applications (132-133) in recent years, particularly automobile and mechanical engineering industry have great interest for short fiber reinforcement in various polymer matrices for better mechanical, dynamic and thermal properties of the concerned composites. Short fiber reinforcement is also favored over the continuous fiber reinforcement because of the combination of easier processability with low manufacturing cost. A large no. of reports is available to analyze the short fiber reinforcement on the mechanical properties of the short fiber reinforced composites (134-135).

Broutman et al (136) have reported about the fibers made of phenol formaldehyde. They have discussed about the properties of molded polypropylene thermoplastics as a function of phenolic fiber weight percent and surface treatment. Sudarisman et al (137) have demonstrated the compressive failure of unidirectional hybrid fiber-reinforced epoxy composites containing carbon and silicon carbide fibers. Arikan et al (138) have reported the fracture behavior of steel fiber reinforced polymer composites. Fu et al (139) demonstrated the thermal conductivity of misaligned short-fiberreinforced polymer composites. They have used carbon fibers as reinforcements. Wang et al (140) have analysed the toughness characteristics of synthetic fibre-reinforced cementitious composites. again, Wang et al (141) have performed an experimental study of synthetic fiber reinforced cementitious composites. They have demonstrated the tensile properties of concrete reinforced with acrylic, nylon, and aramid fibers, in the form of random distribution or unioxial alignment, by means of three different tests: compact tension, flexural, and splitting tensile tests. Parmar et al (142) have reported about the Vinyl ester-based three-component interpenetrating polymer network for glass fiber reinforced composite applications. They have used vinyl ester of an epoxy novolac resin (VEN), diglycidyl ether of bisphenol-A (DGEBA) (an epoxy resin), and methyl methacrylate (MMA) (a vinyl

monomer) as three-component interpenetrating polymer network (IPN) matrix based glass fiber reinforced composites. 2, 2'-Azobisisobutyronitrile (AIBN) has also been employed as the initiator for both MMA and vinyl ester (VEN) resins, while DDM (diamino diphenyl methane) has been employed for curing of DGEBA. The composites are found to have good resistance to chemical reagents, good thermal stability, and good mechanical properties. Li et al (143) have reported about the compressive and flexural behavior of ultra-highmodulus polyethylene fiber and carbon fiber hybrid composites with different hybrid ratios. They have found that the incorporation of a moderate amount of carbon fiber into a UHMPE-fiber-reinforced composite greatly improves the compressive strength, flexural modulus and flexural strength while the addition of a small amount of UHMPE fiber into a carbon-fiber-reinforced composite remarkably enhances the ductility with only a small decrease in the compressive strength.

Kevlar, poly-*p*-paraphenylene terephthalamide (PPTA), is an organic synthetic fiber with a distinct chemical composition of wholly aromatic polyamides (aramids). This fiber possesses a unique combination of high tensile strength and modulus, toughness, and thermal stability (144). In air, PPTA demonstrates seven times the tensile strength of steel on an equal weight basis. In seawater, this advantage in tension increases by a factor of twenty (145). Besides, Kevlar fiber possesses high thermal resistance and chemical inertness and low electrical conductivity with compared to metallic or carbon glass fibers. These superior properties of Kevlar fiber lead to the increasing applications of Kevlar fiber reinforced composites in aircraft, missile and space applications such as rocket motor casings and nozzles. Kevlar fiber composites are also used in conjunction with aluminium to give rise to superior hybrid composites. The fiber failure in the longitudinal splitting mode has led to the unique ballistic resistance of Kevlar when used with suitable combination of matrices. Thus the development of Kevlar composites with high strength as well as stiffness, apart from their proven toughness, is highly relevant and significant in the current scenario where the thrust is on good damage tolerance, high strength and stiffness, good hot-wet properties, high fatigue life and low density. The main draw back of the Kevlar fiber reinforcement is poor interfacial adhesion due to its chemical inertness and low surface energy, which affects the chemical and physical properties of the composites.

In order to increase the surface adhesion of the fiber resulting good interaction with the matrix various physical and chemical surface modification techniques are being followed in present days, which have discussed in section (1.7.1.ii). Moreover, Kalantar et al (146) has reported the bonding mechanism of aramid fibers to epoxy matrices. Takata er al (147) have demonstrated that the increasing aramid-matrix adhesion may improve the compressive strength of aramid composites by deterring the onset of fiber buckling. Morgan et al. (148) Chiao et al. (149), and Chatzi and Koenig (150) have reviewed the properties and morphology of the aramid fibers and their composites. Kompaniets et al. (151) have demonstrated that for the aramid fibers the fiber tensile strength is gauge-length dependent, but for the unidirectional composites the tensile strength is independent of the gauge length. This

observation suggests a different failure mode for the embedded fibers which experience the load transfer by interfacial shear.

Li et al. (152) have studied the wettability of aramid fibers by both the Wihelmy and the solidification front techniques. The Wihelmy technique yielded 43.7mNm⁻¹ values for the surface energies of aramid fibers. Solidification front measurement resulted in 46:4mNm⁻¹ for aramid fibers. Using contact angle analysis, Penn et al (153) have also determined similar surface energies for carbon and aramid fibers. Maalej et al (154) demonstrated the Tensile properties of short fiber composites with fiber strength distribution. They have analyzed the The influence of fiber rupture, fiber pull-out and fiber tensile strength distribution on the post-cracking behavior of short-randomlydistributed fiber reinforced brittle-matrix composites has been analyzed using an approach based on the Weibull weakest-link statistics. Yu et al (155) have predicted the mechanical properties of short Kevlar fiber-nylon-6, 6 composites. Sun et al (156) have reported shear-induced interfacial structure of isotactic polypropylene (iPP) in iPP/Fiber composites, where they have studied the shear-induced interfacial structure of iPP in pulled iPP/fiber composites optical microscopy. Shaker et al (157) have compared the low and high velocity impact response of Kevlar fiber reinforced epoxy composites. Kutty et al (158) have reported the mechanical and dynamic properties of the Short Kevlar fiber-thermoplastic polyurethane composites. Murat İçten (159) have studied the failure analysis of woven Kevlar fiber reinforced epoxy composites pinned joints. Kim et al (160) studied the graft copolymerization of the ε caprolactam onto Kevlar-49 fiber surface and properties of grafted Kevlar fiber

reinforced composite. Haris et al (161) studied the thermal conductivity of the Kevlar fiber reinforced composites. Zhou et al (162) proposed an experimental study on the tensile behavior of Kevlar fiber reinforced aluminium laminates at high strain rates. They have reported that yield strength, tensile strength and failure strain of the composite all increased with increasing strain rate. Takayanagi et al (163) reported about the surface modified Kevlar fiber reinforced polyethylene ionomer. They have modified the poly(*p*-phenylene terephthalamide) (PPTA) surface by the polymer reaction via the metalation reaction in demethyl sulfoxide to provide the fiber surface with several functional groups such as the *n*-octadecyl group, carboxymethyl group, and acrylonitrile and also noticed the enhanced mechanical properties. Iyengar (164) have demonstrated the adhesion of Kevlar fiber to rubber matrix.

They have developed the adhesion between the aramid cords with rubber by using epoxy/RFL adhesives. Al-Bastaki et al (165) have designed the kevlar fiber reinforced epoxy tubes subjected to high strain rates using finite element analysis. Kodama et al (166) demonstrated the Polar-polar interaction between the reinforcement and matrix for Kevlar fiber-reinforced composite: Effect of using the blend of polar polymers as matrix. They have used poly(hydroxy ether of bisphenol A) (I), with which poly(ethylene oxide) (II) or poly(ethylene adipate) (III) was blended as a part of matrix in Kevlar fiber reinforced composites. It is shown by analyzing the storage modulus and loss modulus vs. temperature curves that the reinforcement-matrix interaction is increased relatively to the primary transition temperature of matrix by blending II or III with I, and II is more efficient for increase of the interaction than III. Mahmoud et al (167) have discussed the tensile, impact, and fracture toughness behavior of unidirectional, chopped, and bidirectional fiber reinforced glass and Kevlar/polyester composite in terms of fiber volume fraction and fiber arrangement. Wu et al (168) demonstrated the interfacial studies on the surface modified aramid fiber reinforced epoxy composites. They have used solutions of rare earth modifier (RES) and epoxy chloropropane (ECP) grafting modification method were used for the surface treatment of aramid fiber. Kitagawa et al (169) have evaluated the interfacial property in aramid fiber reinforced epoxy composites. Haque et al (170) have reported the moisture and temperature induced degradation in tensile properties of Kevlar-graphite/epoxy hybrid composites.

In our study surface modification of Kevlar was carried out by fluorination and oxy-fluorination. For effective composites matrix should be well established, economic and easily available and for that purpose ethylene propylene (EP) copolymer, syndiotactic polystyrene (s-PS) and Polycarbonate (PC) have been used as matrix resin for Kevlar fiber reinforcements. Liquid Crystalline polymer (Vectra C) has also been used as processing aid as well as reinforcement in PC matrix.

1.10. Objectives and scope of the work:

Polymer composites offer huge applications in every aspect of life in recent state of affairs. Among various types of composites fiber reinforcements play an important role because of possessing highly favorable mechanical properties, superior strength-to-weight ratios to those of most alloys. When compared to metals they offer many other advantages as well, including noncorrosiveness, translucency good bonding properties, and ease of repair. They also offer the potential for chair side and laboratory fabrication.

Fiber reinforcements are categorized under synthetic and natural fiber reinforcements, which can be further classified into short and long fiber reinforcements.

Short fiber reinforcements possess processing advantages, superior mechanical properties and reduction of cost in processing in comparison to the long fiber reinforcements. Although natural fibers are easily available and cost effective, renewable and biodegradable, they have some disadvantages too. They are hydrophilic in nature and possess poor wettability with matrix composites, lower resistance to moisture uptake, and poor weathering behavior and low mechanical properties. Besides synthetic fibers exhibit superior mechanical properties, dimensional stability, and better weathering characteristics. Synthetic fibers are less hydrophilic in nature and more compatible with hydrocarbon polymeric matrices, which offer them as suitable reinforcing agents in polymeric composites. Among various synthetic fibers pphenylene terepthalamide (i.e. Kevlar) is very much well known for high performance composite applications, because of its high specific strength, high modulus with a high thermal resistance and chemical inertness and low electrical conductivity with compared to metallic or carbon glass fibers.

Another main constituent of the fiber reinforced composites is the matrix, which binds the fibers in their proper position. Hence matrix should be easily available, cost effective and well established. For this purpose in our study Ethylene propylene copolymer (EP), Syndiotactic polystyrene (s-PS) and Polycarbonate have chosen for the short Kevlar fiber reinforcement. Blending of PC with LCP has also been performed to improve the processibility of the Kevlar fiber reinforce PC/LCP blends.

The properties of the short fiber reinforced composites depend on various factors such as fiber/matrix adhesion at the interface, the properties of the constituent materials, fiber orientation and dispersion and fiber aspect ratio. The main factor among this is fiber/matrix adhesion at the interface. In order to improve fiber adhesion various physico-chemical techniques have been followed. But in our study we surface fluorination and oxy-fluorination has been used as effective tool for this purpose as it possess high thermal stability, chemical inertness, better wettability, adhesion properties.

Fiber orientation is also an important governing factor for fiber reinforced polymer composites. In our study we have also reported the simulation of fiber orientation on s-PS/ surface modified and unmodified Kevlar composites under different injection molding condition.

Research objective #1

Many studies have been reported on the Kevlar fiber reinforcements and their surface modifications. Despite this large volume of results, no works have been reported on the fluorination and oxy-fluorination as the Kevlar fiber surface modification tool. Therefore, the first objective is: Development of fluorinated and oxy-fluorinated short Kevlar fiber reinforced thermoplastic composites

Research objective #2

As mentioned earlier (in section 1.8), that fluorination and oxyfluorination enhances the adhesive properties of the polymeric materials. Section 1.7 and 1.8 has described that the surface modification of fibers as well as matrix can be modified by introduction of reactive groups or by addition of a third component to achieve better fiber/matrix adhesion at the interface for different thermoplastic/ fiber composites. Hence our second objective is:

Perform a comprehensive characterization namely IR, DSC, DMTA and SEM to study the fiber/matrix adhesion at the interface.

Research objective #3

Prediction of fiber orientation in the fiber reinforced composites is one of the most important factors to evaluate the properties of those particular composites. The fiber orientation as well as the various physico-chemical properties of the injection molded fiber reinforced composites depends on the processing parameters. Fiber orientation is different in the skin and the core region for that particular composite under different processing conditions. Hence the third objective is:

Simulation of fiber orientation in the short Kevlar fiber reinforced composites by moldflow technique and various physico-chemical properties under different processing parameters.

Chapter: 2

Materials and Experimental Techniques



The details of the materials used and the experimental techniques followed in the present investigation are presented in this chapter

2.1. Materials Used:

2.1.1. Ethylene propylene copolymer (Thermoplastic) (EP):

Ethylene propylene copolymer is an easily available and economic polymeric composite. It is thermoplastic in nature. It possesses better resistance to stress cracking than Polyethylene or Polypropylene, superior low temperature toughness compared to Polypropylene or Polyethylene. It also exhibits better fatigue resistance than Polypropylene. It possesses low density than the constituent polymeric material. Main disadvantage of this polymer is its low surface hardness.

The thermoplastic ethylene propylene polymer was procured from IPCL, India. It contains 90 % propylene and 10 % ethylene.

$$- \begin{array}{c} - CH_{2} - CH_{2} \\ - CH_{2} \\ - CH_{2} \\ - CH_{3} \\ - CH$$

x:y = 10:90
2.1.2. Maleic anhydride grafted polypropylene (MA-g-PP):

Maleic anhydride grafted polypropylene recommended as a coupling agent for polypropylene (PP) composites because of the polarity and anhydride functionality.

The MA-g-PP's ability to enhance the composite properties depends on many factors, such as type of MA-g-PP (graft level, random or block copolymer, molecular weight), miscibility of MA-g-PP with the PP matrix, PP grade, composite processing conditions. Maleic anhydride grafted Polypropylene (PP-g-MAH, Fusabond[®] P MD511 D) in this study was supplied by Du Pont.



2.1.3. p-Polyphenylene terephthalamide (Kevlar):

Kevlar is the DuPont Company's brand name for a particularly light but very strong synthetic fiber. It wad created in DuPont's labs in 1975 by Stephanie Kwolek and Herbert Blades, Kevlar was first used commercially in the early 1980s. Kevlar's structure consists of relatively rigid molecules, which tend to form mostly planar sheet-like structures that have similarities to silk protein. It possesse extremely high strength, high modulus and dynamic stability. Kevlar derives a portion of its improved strength from intermolecular hydrogen bonds formed between the carbonyl groups and protons on neighboring polymer chains and the partial pi stacking of the benzenoid aromatic staking interaction between stacked strands. These interactions have a greater influence on Kevlar than van der waals interactions and chain length that typically influence the properties of other synthetic polymers and fibers like Dyneema. This type of chemical structure makes it chemically inert.

Kevlar (p- Polyphenylene terephthalamide, 1100 dtex) used in our study was supplied by DuPont, USA.



2.1.4. Syndiotactic polystyrene (s-PS):

Syndiotactic polystyrene (s-PS) is a semicrystalline polymer synthesized from styrene monomer using a single-site catalyst, such as metallocene. First synthesized in 1985 by Idemitsu Kosan Co. Ltd. (Tokyo, Japan), the material has been under joint product and process development by Idemitsu and Dow Plastics (Midland, MI) since 1988. Because of its semicrystalline nature, s-PS products exhibit performance attributes that are significantly different from those of amorphous styrenic materials. These properties include a high melting point, good chemical and moisture resistance, and a high degree of dimensional stability.

Syndiotactic polystyrene used in this study was obtained from Polyone, Germany.



2.1.5. Poly carbonates (PC):

Polycarbonates are a particular group of thermoplastic polymers. They are easily worked, molded, and thermoformed; as such, these plastics are very widely used in the modern chemical industry. Their interesting features (temperature resistance, impact resistance and optical properties) position them between commodity plastics and engineering plastics.

Polycarbonate was procured by Macrolon, Bayer Material Science, West Germany.



2.1.6. Liquid Crystalline Polymer (LCP):

Liquid crystalline polymers exhibit a phase intermediate to the isotropic liquid and solid crystal state called a mesophase. It is again divided into three parts depending on type of ordering. Majority of the LCPs are copolyester, co polyamides and polyester amides. Recently two main types of thermoplastic LCPs are available in market- Vectra and Xydar.

LCPs possess some excellent properties like high heat resistance, flame retardant, chemical Resistance, dimensional Stability, moldability, heat aging resistance, adhesion,

low viscosity, low cost and over all they act as viscosity reducing agent.



x:y= 80:20

2.2. Preparation of composites:

2.2.1. Modification of fibers:

Kevlar fibers (1100 dtex) were modified by fluorination and oxy-fluorination separately.

Fluorination was carried out using a gaseous mixture of fluorine and helium (F₂: He=5%: 95%) at 0.4 bar total pressure during ~1 hour at 17^{0} C.

Oxy-fluorination was done by a gaseous mixture of fluorine, air (containing 4% nitrogen and 1% oxygen) and helium (5%, 5% and 90%) under 0.8 bar pressure and at 17^{0} C for 30 minutes.

2.2.2. Mixing process:

In our study we have used brabender mixer and twin screw extruder for the purpose of mixing of different polymeric materials which we will discuss later.

2.3. Physical Test Method:

For the tests described below specimens were tested for measurement of each property and the mean values were reported.

2.3.1. Molding of the test blend samples:

The molding of the test samples was done using compression molding and injection molding machine differently which will be discussed later.

2.3.2. Elemental analysis (C H N S/O):

Elemental analysis is an experiment that determines the amount (typically a weight percent) of an element in a compound. Just as there are many different elements, there are many different experiments for determining elemental composition. The most common type of elemental analysis is for carbon, hydrogen, nitrogen, sulfur and oxygen (CHN analysis). This type of analysis is especially useful for organic compounds (compounds containing carbon-carbon bonds).

The elemental analysis of a compound is particularly useful in determining the empirical formula of the compound. The empirical formula is the formula for a compound that contains the smallest set integer ratios for the elements in the compound that gives the correct elemental composition by mass.

C, H, N, O analysis in our study was carried out using CHNS/O analyzer (Perkin Elmer Instruments, Series II). Fluorine was determined as the balance of the CHN analysis and the results obtained from this experiment are tabulated in Table 2.1.

Table 2.1: CHNS/O analysis of original (KO), fluorinated (KF) and oxy-fluorinated Kevlar fiber:

Sample Code	<u>C (%)</u>	<u>H (%)</u>	<u>N (%)</u>	<u>O (%)</u>	<u>F (%)</u>
КО	68.25	4.65	11.12	15.98	-
KF	68.00	3.51	10.97	15.69	1.83
KOF	67.42	3.00	11.15	16.51	1.92

2.3.3. Fourier Transformation Infrared spectroscopy (FTIR):

FTIR spectroscopic analysis is a widely used analytical tool for characterization of polymers. The major applications of FTIR in polymer analysis include the following:

- i) Polymer identification
- ii) Determination of chain branching and end groups
- iii) Assessment of polymer degradation
- iv) Determination of polymer crystallinity
- v) Degree of cure of cross linked structure

FTIR of original and treated Kevlar fiber and also the composites materials was done using a NEXUS 870 FTIR (Thermo Nicolet) in humidity free atmospheres at room temperature to understand the chemical bonding formed due to the treatment of the materials.

2.3.4. X-ray Diffraction analysis (XRD):

In addition to inelastic absorption phenomena, elastic interaction between EM radiation and a material is possible and this gives rise to diffraction and scattering phenomena. The small crystallite size and dominance of crystalline orientation in processed plastics lead to several unique analytic approaches in the analysis of x-ray diffraction data in these materials. The focus in this course will be on those tools used in diffraction, which are specific to polymeric materials. Small-angle x-ray scattering is a critical technique for the description of polymeric materials since diffraction at small angles is associated with the colloidal to nano-scales, which is the size range of a typical polymer chain. The colloidal scale is also associated with polymer crystallites (lamellae) and microphase separated block copolymer structures. Further, light scattering has been widely used in polymer science to describe disordered micron scale structure as well as a primary technique for the determination of molecular weight from dilute solutions.

X-ray diffraction was studied using PW-1840 X-ray diffractometer with Cu-K_{α} and Co-K_{α} targets at 2mm slit. X-ray diffraction study was carried out to get an idea of the crystallinity of the blends as affected by blend ratios The area under crystalline and amorphous portion was determined in arbitrary units. The degree of crystallinity χ_c and the amorphous content χ_a was measured, using relationship:

$$\chi_c = I_c / (I_a + I_c) \dots 2.1$$
; $\chi_a = I_a / (I_a + I_c) \dots 2.2$

Where, I_c and I_a are the integrated intensities corresponding to the crystalline and amorphous phase respectively. The crystallite size (P) and interplaner distance (d) were calculated as follows,

 $P = K\lambda / \beta \cos\theta \dots 2.3$ $d = \lambda / 2 \sin\theta \dots 2.4$

Where β is half height width (in radian) of the crystalline peak and λ is the wavelength of the X-ray radiation (1.548 for Cu and 1.79 for Co) and K is the Scherrer constant taken as 0.9(171, 172).

2.3.5. Differential Scanning Calorimetry (DSC):

Differential Scanning Calorimetry (DSC) is a widely used technique for determining the thermal behavior of the polymeric species i.e., melting temperature (T_m), glass transition temperature (T_g) and more over the crystalline behavior of the polymer sample such as degree of crystallinity, crystallization temperature (T_c), heat of fusion and degree of cure of polymer samples.

DSC is a dominant technique for the thermal analytical investigation. It measures the difference in energy inputs into a substance and reference materials as they are subjected to a controlled temperature programme practically all physical and chemical process involve the changes of enthalpy or specific heats. Thus the heat of transition is determined by integrating the heat (energy) input over the time removal covering the transition, which is recorded in Perkin-Elmer PYRIS Diamond and NETZSCH DSC 200 PC instrument in presence of nitrogen with in the range of 25^oC to 300^oC at a heating rate 10^oC/min.

2.3.6. Thermogravimetric analysis (TGA):

Thermogravimetric Analysis or TGA is a type of characterization that is executed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

TGA studies were carried out Shimadzu-DT-40 and NETZSCH TG 209F1 instrument in presence of air at a rate of 10° C/min from 25° C to 600° C temperature Degradation temperature of the composites was calculated by TGA plot.

2.3.7. Rheology study:

Rheology is defined as the flow of fluids and deformation of solids under stress and strain. Rheometers are the instruments used to measure a material's rheological properties. There are many types of rheometers that are available with the most versatile being controlled stress and/or strain rheometers and capillary rheometers. Rheology study includes the measurement of viscosity as a function of shear rate to determine non-Newtonian flow behavior, as well the complex rheological properties such as viscoelasticity (G', G'') as a function of frequency (time) or temperature.

The rheology of polymers and plastics are critical for determining molecular architecture, processing behavior, and end product performance. Rheological parameters of the composites were studied with the help of

Dynamic analyzer RDA-II (Rheometrics Inc., USA) equipped parallel plate. All measurements were carried out at temperatures 200° C and 320° C and a shear rate range of 1-100 s⁻¹.

2.3.8. Dynamic Mechanical Thermal Analysis (DMTA):

Dynamic mechanical study was performed in a TA instrument DMA 2980 dynamic mechanical analyzer in bending single cantilever mode. The samples are subjected to a sinusoidal displacement 0.1% strain rate at a frequency of 1Hz with a heating rate of 10^{0} C/min. The temperature dependence of storage modulus E', loss modulus E'' and loss tangent (tan δ) was measured from $+25^{0}$ C to $+250^{0}$ C with a heating rate 10^{0} C/min. The specimen of dimension 46mmX13mmX4mmcut from the molded slab was used for dynamic mechanical thermal analysis. The storage modulus, loss modulus, stiffness and a mechanical damping or internal frictions express these properties. These dynamic parameters were used to determine the glass transition region, relaxation spectra, cross linking and phase inversion of polymer blends.

2.3.9. Scanning Electron Microscopic Study (SEM):

The study of fracture mechanism was carried out on tensile and cryo fractured surface of the samples. The tensile fracture surfaces of the samples were carefully cut out from the test specimen and were auto sputtered coated with gold for the nonconducting nature of the polymer at 0^0 tilt angle for the morphological study. The SEM examination was conducted always the day after the gold coating of the samples. In the present work SEM investigations were done using JSM-5800 of JEOL Co.

2.3.10. Mechanical Properties measurements:

Mechanical properties of samples were measured at room temperature using a tensile tester [OUNSFIELD (model H10KS)]. The gauge length and crosshead speed were 35 mm and 5 mm/min, respectively and fiver measurements were taken for the accuracy.

Impact testing was performed for the composite samples of the same dimensions using a ZWI CK 51 02 charpy test machine and also five measurements were taken.

2.3.11. Atomic Force Microscopic (AFM)

AFM measurements were conducted using an atomic force microscope (Digital Instrument, Nanoscope IIIa, USA) at room temperature. The cantilever used in this study is triangular one with micro fabricated silicone nitride (Si_3N_4) micritip (Olympus Co.) and with spring constant of 0.022 N/m. The scanning direction was perpendicular to the long axis of the cantilever. The experiments were carried out in the phase imaging mode. Phase imaging is a powerful extension of TappingMode that provides nanometer scale information about surface structure. In phase imaging, the phase lag of the cantilever oscillation, relative to the signal sent to the cantilever's piezo driver, is simultaneously monitored by the Extender Electronics Module and recorded by the Nanoscope III SPM controller.

Chapter: 3A

Effect of Fluorinated and Oxy-fluorinated Short Kevlar Fiber on the Properties of Ethylene Propylene Matrix Composites Effect of fluorinated and oxy-fluorinated short Kevlar fiber on the properties of ethylene propylene matrix composites

Three samples along with the neat polymer were prepared to study the effect of fluorinated and oxy-fluorinated short Kevlar fiber reinforcements on the properties of the ethylene propylene matrix composites. The compounding formulations are tabulated in the Table 3A.1

Sample Code	EP (%)	Kevlar (%)
EP	100	0
В	100	1.43 (original)
Е	100	1.43 (fluorinated)
Н	100	1.43 (oxy-fluorinated)

Table 3A.1: Compounding formulations:

3A.1. Preparation of the composites:

Ethylene polypropylene in 100% was mixed with 1.43% original, fluorinated and oxy-fluorinated Kevlar differently in Brabender mixer with 60 rpm at 200° C temperature for 10 min. Then the mixtures were molded in hydraulic press at 200° C and at 10 MPa pressure for 10 minutes.

3A.2. FTIR study:

The FTIR spectra of the composite materials along with the pure EP are represented in Figure 3A.1. The peak associated with primary amine backbone appeared in the cases of B, E, and H, at 3340 cm⁻¹(173) but in the case of pure EP these peaks are totally vanished, which may be due to the incorporation of Kevlar fiber into the polymer matrix.

The peak at 1760 cm⁻¹ in the case of B, E, H showed the characteristic peaks of C=O stretching frequency of Kevlar fiber. The FTIR picture of E and H showed the peaks at 1200 cm⁻¹, which may be the characteristic peak of monofluorinate aliphatic groups (C-F bond), formed due to the fluorination and oxy-fluorination.



Figure 3A.1: FTIR spectra of Pure EP (EP), Kevlar fiber reinforced EP (B), Fluorinated Kevlar fiber reinforced EP (E) and Oxy-fluorinated Kevlar fiber reinforced EP (H)

The figure representing H showed an additional peak at 3400 cm⁻¹ representing OH group, arises due to oxy-fluorination of the Kevlar fiber.

3A.3. Thermal Properties:

To study the decomposition pattern and thermal stability of the EP, EP/Kevlar differential composites. scanning calorimetry (DSC) / thermogravimetric analyzer (TGA) measurements were carried out. The DSC/TGA plots of pure EP and EP/Kevlar composites are shown in Figure 3A.2 and 3A.3 and the respective parameters are summarized in Table 3A.2. It was observed from Table 3 that heat of fusion is highest for pure EP and then decreases gradually in case of fiber reinforced composites, which supports the trend of crystallinty of the blends obtained from the XRD study. Heat of fusion is proportional to the amount of crystallinity in the sample, which follows the results of X-ray diffraction study. Pure EP shows a melting endotherm, T_m, at about 165°C and the composites showed the values close to the T_m of EP $(B=162.3^{\circ}C, E=162.4^{\circ}C, and H=164.1^{\circ}C)$. The melting point of EP, however, marginally decreases in case of composites. The depression of the melting temperature of the composites is due to the dilution effect.



Figure 3A.2: DSC study of Pure EP (EP), Kevlar fiber reinforced EP (B), Fluorinated Kevlar fiber reinforced EP (E) and Oxy-fluorinated Kevlar fiber reinforced EP (H)

In case of all EP and EP/Kevlar composites, the degradation mainly occurs in two steps. In case of EP, the initial degradation starts at 233°C and continues up to 387°C at a faster rate accompanied by 69% degradation. The second degradation step starts at 387°C and found to proceed at a slower rate. For EP/Kevlar composite (sample B) the degradation starts at 245°C and continues up to 352°C at a slowest rate and almost 32% of the sample degraded in this step. However, in case of EP/Kevlar (fluorinated) and EP/Kevlar (oxy-fluorinated), the initial degradation starts at a higher temperature (about 254.4°C, 269°C) than B. This first degradation process is slower than pure EP and associated with 39% and 54 % sample degradation, respectively.

Sample	1st decom. Temp. (°C)	Loss of Wt. (%) for 1st	2nd decom. Temp. (°C)	Loss of Wt (%) for 2nd	T _m (°C)	H _f (J/g)
		step.		step.		
EP	233.0	69.2	387	30.8	165.0	73.0
В	245.0	32	352	68	162.3	69.2
2	2.0.0	02	002	00	102.0	
Е	254.4	39	352	61	162.4	68.5
Н	269.0	54	391	38	164.1	70.0
11	207.0	54	571	50	107.1	70.0

Table3A.2: Thermal parameters of EP, EP/Kevlar composites:



Figure 3A.3: TG study of Pure EP (EP), Kevlar fiber reinforced EP (B), Fluorinated Kevlar fiber reinforced EP (E) and Oxy-fluorinated Kevlar fiber reinforced EP (H)

This result of TGA implies that due to incorporation of functional group into Kevlar fiber enhances the compatibility of two polymeric species leading to higher thermal stability in case of fluorinated and oxy-fluorinated Kevlar Fiber/EP composites. It is important to point out that the extent of more interaction due to more functional groups of oxy-fluorinated Kevlar fiber can be responsible for a higher thermal stability of the oxy-fluorinated Kevlar fiber reinforced (H) composite as oxy-fluorination generates controlled amount of long-living RO_2^* radical (88, 90-92, 174). These radicals further may be responsible for graft polymerizations leading to the highest thermal stability of H amongst all the composites resulting good adhesion between fiber and the matrix. The effect of interaction becomes more influential over crystallization effect.

3A.4. X-ray study:

X-ray diffraction (XRD) diagram of various samples were displayed in Figure 2 and the respective parameters were shown in Table 3A.3. From Figure 3A.4, it can be revealed that the percent crystallinity is the highest for pure EP and the lowest for Kevlar fiber. The pure EP and Kevlar showed 76% and 30% crystallinity, respectively. The percentage of crystallinity significantly changes with the addition of Kevlar fiber into the EP matrix.



Figure 3A.4: XRD pattern of Pure EP (EP), Kevlar fiber reinforced EP (B), Fluorinated Kevlar fiber reinforced EP (E) and Oxy-fluorinated Kevlar fiber reinforced EP (H)

The Kevlar fiber hinders the migration and diffusion of EP molecular chains to the surface of the growing polymer crystal in the composites, resulting in a decrease in the percent crystallinity.

Tuble efficities for the und the file that composites																
		Peak angle					Interplaner			Crystallite Size (Ao)				A 0)		
ode linity	(20 in degree)						Distance (Ao)									
Sample c	% Crystal	θ_1	θ_2	$ heta_3$	$ heta_4$	$ heta_5$	\mathbf{d}_1	d_2	d_3	d_4	d_5	p_1	p_2	p_3	p_4	p5
EP	74.00	14.20	16.95	18.70	21.30	21.90	6.26	5.25	4.76	4.12	4.18	116.60	164.60	165.30	137.80	137.90
Kevlar	30.00	ı		ı	20.58	22.80	·		•	4.45	3.91		ı		46.40	39.50
В	52.00	14.20	17.0	18.70	21.32	21.88	6.26	5.23	4.76	4.18	4.06	144.70	156.40	145.60	102.30	102.40
Щ	58.00	14.20	17.05	18.68	21.34	21.95	6.26	5.22	4.77	4.18	4.06	144.70	145.20	146.70	120.30	120.50
Н	60.00	14.10	16.90	18.66	21.20	21.88	6.31	5.23	4.80	4.02	4.08	155.80	156.40	145.50	113.60	114.10

Table 3A.3: X-ray parameters of EP and EP/Keylar composites

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Ch-3A: Effect of Fluorinated and Oxy-fluorinated

In the case of composite E and H, the percent crystallinity increases with fluorination and oxy-fluorination in the composites compared to the composite B. These suggested that there are more interactions between the Kevlar fiber and EP matrix. This is due to the generation of more functional groups onto the surface of Kevlar fiber during fluorination and oxyfluorination. It is also important to point out that the crystallite size of composites E and H correspond to all peak angles (2 θ) are higher than composite B, which suggested that the nucleation and growth are also favored in case of E and H compared to B. The pure EP showed the reflection at 2 θ 's of 21.6° and 24.0°, whereas Kevlar fiber showed the reflection at 20.6, 22.8, and 28.7°. In composites, the peak of EP at 24.0° and Kevlar at 28.7° were not visible, but three additional broad peaks are appeared. As the functional groups increased, the intensity and sharpness also increased in the case of modified Kevlar fiber reinforced composites. However, significant changes in the EP crystalline structure were observed in the presence of Kevlar fiber.

3A.5. Dynamic Mechanical Thermal Analysis (DMTA):

Figure 3A.5 Represents the storage modulus E['], for the EP, EP –Kevlar composites with and without fluorination of Kevlar. The storage modulus of the composites decreases with increasing temperature due to an increase in the segmental mobility. The all Kevlar filled EP composites show higher storage modulus than pure EP. This may be due to the reinforcement imparted by Kevlar fibers that permits stress transfer from the EP matrix to Kevlar fiber.



Figure 3A.5: Storage modulus vs. temperature curve of Pure EP (EP), Kevlar fiber reinforced EP (B), Fluorinated Kevlar fiber reinforced EP (E) and Oxy-fluorinated Kevlar fiber reinforced EP (H)

The storage modulus increases especially in the glass region in case of oxy-fluorinated Kevlar fiber reinforced EP composites due to the increase in functional groups. It can be explained by the fact that the functional groups affect the surface characteristics of Kevlar fibers, resulting in improved interfacial adhesion between the fibers and matrix, which reduces molecular mobility of EP. The storage modulus graphs show a sharp decrease in the temperature range 0 to 10°C, which correlates with the glass transition temperature.

The tan δ versus temperature curve is represented in Figure 3A.6. It is clearly observed in Figure 6 that one relaxation peak appears at around 10°C which is α -transition of EP polymer (175). The α -transition shifted to higher temperatures for all the composites due to the presence of Kevlar fiber in the EP matrix, which tends to decrease the mobility of the matrix chains. The loss peaks were indicative of the efficiency of the material in dissipating mechanical energy. The magnitude of the loss peak was lower in case of sample H. The lower magnitude of loss peak indicated lower mechanical energy dissipation capacity.



Figure 3A.6: Tan delta vs. temperature curve of Pure EP (EP), Kevlar fiber reinforced EP (B), Fluorinated Kevlar fiber reinforced EP (E) and Oxy-fluorinated Kevlar fiber reinforced EP (H)

Hence, the molecular mobility of the composites decreases and the mechanical loss is reduced after incorporating the oxy-fluorinated Kevlar fibers to EP matrix. This can be also pointed out that the transition peak progressively broadens. The broadening of loss peak in the presence of fiber can be ascribed to matrix-fiber (filler) interaction. The matrix polymer in the adjacent portion of the fiber can be considered to be in different state in comparison to the bulk matrix, which can disturb the relaxation of the matrix resulting in a broad tan δ peak (158).

3A.6. Mechanical Properties:

Mechanical properties of composites along with the matrix polymer are given in Table 3A. The matrix shows higher tensile strength and high elongation at break compared to EP/Kevlar composite. This arises from the very basic ordered structure of EP, which is also evident from % crystallinity value obtained from XRD study mentioned earlier. The mechanical properties like modulus and tensile strength of polymeric materials strongly depend on their microstructure and crystallinity. So, crystallinity enhances the tensile properties of pure EP. The tensile strength decreases sharply on addition of Kevlar fibers (sample B) into the polymer matrix i.e. EP as compared to neat polymer matrix (EP) whereas it increases gradually in case of fluorinated Kevlar fiber/EP (sample E) and oxyfluorinated Kevlar fiber/EP composites (H). The observed strength in the presence of fiber is due to the result of two opposing effects: dilution of the matrix and the reinforcement of the matrix by fibers. In case of sample B the matrix is not properly restrained by fibers because of poor adhesion between the fiber and matrix and concentration of the localized strains on the matrix, causing the pulling out of fibers and leaving the matrix diluted by non-reinforcing, debonded fibers. But in the case of E and H, where the matrix is sufficiently restrained and the stress is more evenly distributed.

Sample	Tensile	Elongation at	Tensile
-	Strength (MPa)	break (%)	Modulus (GPa)
Pure EP (EP)	27	125	$0.36~\pm~0.03$
В	20	6.85	$0.40~\pm~0.02$
Е	30	5.13	$0.56 \ \pm \ 0.02$
Н	33	4.02	0.68 ± 0.01

Table3A.4: Mechanical properties of EP, EP/Kevlar composites:

This can be ascribed as the functional groups affect the surface characteristics of the fibers which increase the adhesion between the fiber and matrix. This is more prominent in case of H. In these two cases (E, H) the reinforcement effect became more influential over crystallization effect. The reinforcement effect of Kevlar fibers in the EP matrix is also evident from dynamic mechanical analysis, as explained earlier.

3A.7. SEM study:

The homogeneous dispersion of short fibers in the polymer matrix is one of the conditions for a composite to show good mechanical strength reinforcement because inhomogeneities can lead to structural defects in the composite material. Figure 3A.7, showed the SEM images of the crosssectional tensile fracture of EP and EP-Kevlar composites. Figure 3A.7a, showed the tensile fracture of B. In case of B the fibers are randomly oriented and pulled out from the matrix resulting poor adhesion between the fiber and matrix.







b



с

Figure 3A.7: SEM photograph of a) unmodified Kevlar/ EP (B), b) fluorinated Kevlar / EP(E), c) oxy-fluorinated Kevlar / EP (H)

Because the load transfer from the matrix to the fibers is not large enough under tensile loading. As a result the strength of the composite decreases from the pure EP which is in line with the results obtained from the tensile strength of the composites. In case of E, (Figure 3A.7b) fibers are broken rather than pulled out due to the strong interfacial bonding between the fibers and the polymer matrix. In case of H the (Figure 3A.7c) fibers and the matrix forms network giving rise to the best mechanical and thermal properties as a result of good adhesion between fiber and the matrix. This may be due to the incorporation of functionalized Kevlar fibers (i.e. oxy-fluorinated Kevlar fiber).

3A.8. AFM study:

Figures 3A.8, 3A.9 and 3A.10 represent the two-dimensional and three dimensional AFM images of EP-Kevlar (B), EP-fluorinated Kevlar (E) and EP/oxy-fluorinated Kevlar (H) composites.



Figure 3A.8: AFM images of a) two dimensional image of EP/ unmodified Kevlar composite (B), b) Three dimensional image of EP/ unmodified Kevlar composite (B)

Comparison of the AFM topographies of composites with the surface roughness data, however, suggested that the orientation of the Kevlar fiber during the preparation of composite samples might play more active roles in determining the surface morphology. The maximum surface roughness of B, E, and H composites were measured as 4, 17 and 26 nm, respectively. The interface roughness is one of the most important parameter of interface adhesion strength as reported earlier (176).



Figure 3A.9: AFM images of a) two dimensional image of EP/ fluorinated Kevlar composite (E), b) Three dimensional image of EP/ fluorinated Kevlar composite (E)

So, the roughness data strongly suggested that the adhesion strength of oxy-fluorinated Kevlar fiber / EP interface is considerably much higher than of EP/ fluorinated Kevlar and EP/ Kevlar composites.



Figure 3A.10: AFM images of a) two dimensional image of EP/oxy-fluorinated Kevlar composite (H), b) Three dimensional image of EP/ oxy-fluorinated Kevlar composite (H).

Chapter: 3B

Compatibilizing Effect of MA-g-PP on the properties of Fluorinated and Oxy-fluorinated Kevlar Fiber Reinforced Ethylene Polypropylene Composites

Compatibilizing effect of MA-g-PP on the properties of fluorinated and oxy-fluorinated Kevlar fiber reinforced ethylene polypropylene composites

Nine samples are prepared along with the neat polymer were prepared to study the compatibilizing effect of MA-g-PP on the properties of unmodified and modified Kevlar /EP composites. The compounding formulations are given below:

Sample Code	EP (%)	Kevlar (%)	Compatibilizer (%)
EP	100	0	-
В	100	1.43 (original)	-
B1	100	1.43 (original)	2
B2	100	1.43 (original)	5
E	100	1.43 (fluorinated)	-
E1	100	1.43 (fluorinated)	2
E2	100	1.43 (fluorinated)	5
Н	100	1.43 (oxy-fluorinated)	-
H1	100	1.43 (oxy-fluorinated)	2
H2	100	1.43 (oxy-fluorinated)	5

Table 3B.1: Compounding formulation:

3B.1. Preparation of the composites:

Ethylene polypropylene in 100% was mixed with 1.43% of original, fluorinated and oxy-fluorinated Kevlar fiber and 2% and 5% of MA-g-PP as compatibilizer differently in Brabender mixer with 60 rpm at 200° C temperature for 10 min. The compounding formulation is shown in Table 1. Then the mixtures were molded in hydraulic press at 200° C and at 10 MPa pressure for 10 minutes.

3B.2. Thermal Properties:

In order to understand the effect of compatibilizers on the thermal properties of the untreated, fluorinated and oxy-fluorinated Kevlar/EP composites, thermogravimatric (TG) and Differential scanning calorimetric (DSC) study were conducted. The results obtained from the DSC study are tabulated in the Table 3B.2 and displayed in Figure 3B.1 (a-c).

	1^{st}	50%	T _m	$H_{f}(J/g)$
Sample	degradation	degradation	(°C)	
code	Temp. (°C)	Temp. (°C)		
EP	233.0	338.1	165.0	73.0
В	245.0	349.5	162.3	69.2
B1	260.5	365.3	162.9	70.2
B2	263.0	370.9	163.1	71.1
Е	254.4	331.8	162.4	68.5
E1	266.6	346.2	163.1	69.8
E2	272.9	383.3	163.9	70.5
Н	269.0	349.4	164.1	70.0
H1	292.0	374.0	164.8	72.3
H2	295.6	400.0	164.5	72.8

Table 3B.2: Thermal parameters of EP, EP/Kevlar composites:

Table 3B.2 and Figure 3B.1 (a-c) show that on addition of compatibilizer the magnitude of heats of fusion for both the untreated, fluorinated and oxy-fluorinated Kevlar fiber reinforced EP increases in very marginal extent. This enhancement effect is very much pronounced in case of oxy-fluorinated Kevlar/ EP composites. This indicates the interaction between the oxy-fluorinated Kevlar fibers and the matrix as well as between MA-g-PP and EP at interfacial region thus contributing to an increased adhesion.

However, the melting point (T_m) of the composites shifts marginally towards lower value due to the dilution effect of the matrix.



Figure 3B.1.a) DSC study of Kevlar /EP composite (B), Kevlar /EP/ 2% MA-g-PP composite (B1), Kevlar/ EP/ 5% MA-g-PP (B2)



Figure 3B.1.b) DSC study of fluorinated Kevlar /EP composite (E), Kevlar /EP/ 2% MA-g-PP composite (E1), Kevlar/ EP/ 5% MA-g-PP (E2)


Figure 3B.1.c) DSC study of oxy-fluorinated Kevlar /EP composite (H), oxy-fluorinated Kevlar /EP/ 2% MA-g-PP composite (H1), oxy-fluorinated Kevlar/ EP/ 5% MA-g-PP (H2)

But MA-g-PP contents have very little influence (Figure 3B.2 (a-c), and Table 3B.2) on the melting peaks of the both untreated and oxy-fluorinated Kevlar /EP composites, regardless of position and shape of the peaks. The TG curves of the composites obtained at a heating rate 10° C/min in air and are shown in Figure 2a, b and c and respective parameters are tabulated in Table 3B.2. In our previous work (177) it was reported that surface modification of the fibers by oxy-fluorination leads to the enhanced thermal stability of the EP/Kevlar composites. From the figure 2a, b, c and Table 2 it is very much evident that degradation occurs in two steps in case of all composites. As we have mentioned in our earlier work that for pure EP degradation starts at 233° C

(177) and it gradually increases in case of all EP/Kevlar composites especially for modified Kevlar fiber reinforced EP composites (B= 245° C, E= 254.4 and H= 269° C).



Figure 3B.2.a) TG study of Kevlar /EP composite (B), Kevlar /EP/ 2% MA-g-PP composite (B1), Kevlar/ EP/ 5% MA-g-PP (B2)



Figure 3B.2.b) TG study of fluorinated Kevlar /EP composite (E), Kevlar /EP/ 2% MA-g-PP composite (E1), Kevlar/ EP/ 5% MA-g-PP (E2)



Figure 3B.2.c) DSC study of oxy-fluorinated Kevlar /EP composite (H), oxy-fluorinated Kevlar /EP/ 2% MA-g-PP composite (H1), oxy-fluorinated Kevlar/ EP/ 5% MA-g-PP (H2)

It is very interested to note that use of compatibilizers to the aforementioned composites further appreciably increases the thermal stability of the compatibilized systems. From the Figure 3B.2 (a-c) and Table 3b.2 it is again clearly evident that unmodified Kevlar/EP/MA-g-PP composites containing 2% (B1) and 5% (B2) show onset degradation temperature at about 265^oC and 270.7^oC respectively. It is also observed that fluorinated Kevlar/EP and oxy-fluorinated Kevlar/EP composites containing 2% of MA-g-PP show onset degradation temperature at about 266.6^oC and 272.9^oC, 292.0^oC and 295.6^oC respectively. It is clear from these results that thermal stability of the composites increases in case of compatibilized systems in comparison to

the uncompatibilized one. This may be due to the incorporation of the compatibilizer resulting better adhesion between the fiber and the matrix that increases the compatibility between the fiber and matrix giving rise to enhanced thermal stability of the compatibilized systems. Besides, we can also observe that enhancement of thermal stability is more distinct in case of MA-g-PP comapatibilized oxy-fluorinated Kevlar/EP composites (H1, H2) which is ascribed as the better interaction between the fiber and the matrix at the interface arising due to the generation of reactive functional group (peroxy radical) (88, 95) on the Kevlar surface and on that of the matrix as well (due to MA-g-PP) resulting the strong interface. At higher MA-g-PP contents thermal stability of the both unmodified, fluorinated and oxy-fluorinated Kevlar /EP composites increases very marginally.

3B.3. X-ray study:

X-ray diffraction (XRD) patterns of uncompatibilized and compatibilized surface modified Kevlar/EP composites are shown in the Figure 3B.3 (a-c) and the respective parameters are tabulated in the Table 3B.3. From Table 3B.3 it is clear that use of compatibilizer appreciably affect the crystalline properties of the surface unmodified as well as modified Kevlar/EP composites.



Figure 3B.3.a) XRD pattern of Kevlar /EP composite (B), Kevlar /EP/ 2% MA-g-PP composite (B1), Kevlar/ EP/ 5% MA-g-PP (B2)

This may be due to the better interaction between the fiber and matrix surface resulting improved adhesion between them at the interface which in turn favors the crystal growth mechanism. But in all cases the percent crystallinty of the composites are lower than that of the pure EP (177). This may be due to the hindrance offered by Kevlar fiber in the migration and diffusion of the matrix polymer chains to surface of the growing polymer crystal in the composites.

e code	%	Peak angle (2θ in degree)						erpla	iner I (A ^o)	Distar	nce	C	rystal	llite S	Size (A	<u>л°)</u>
Sampl		$\boldsymbol{\theta}_1$	$\boldsymbol{\theta}_2$	$ heta_3$	$ heta_4$	$ heta_5$	d_1	\mathbf{d}_2	d_3	d_4	\mathbf{d}_{5}	\mathbf{p}_1	p_2	p_3	p_4	\mathbf{p}_5
EP	74.00		16.95	18.70	21.30	21.90	6.26	5.25	4.76	4.12	4.18	116.6	164.6	165.3	137.8	137.9
В	52.00	14.20	17.0	18.70	21.32	21.88	6.26	5.23	4.76	4.18	4.06	144.70	156.40	145.60	102.30	102.40
B1	55.00	14.10	16.93	18.57	21.16	21.87	6.30	5.28	4.79	4.21	4.08	146.2	158.1	146.7	104.1	103.9
B2	56.00	14.26	17.01	18.73	21.24	21.95	6.23	5.23	4.75	4.20	4.07	147.3	159.3	147.1	105.0	105.6
Щ	58.00	14.20	17.05	18.68	21.34	21.95	6.26	5.22	4.77	4.18	4.06	144.70	145.20	146.70	120.30	120.50
E1	59.00	14.10	16.93	18.57	21.08	21.79	6.30	5.25	4.79	4.23	4.09	145.3	146.6	147.8	121.5	121.8
E2	61.00	14.18	16.93	18.57	21.08	21.79	6.27	5.23	4.77	4.20	4.07	146.53	148.01	150.12	122.79	122.03
Н	60.00	14.10	16.90	18.66	21.20	21.88	6.31	5.23	4.80	4.02	4.08	155.80	156.40	145.50	113.60	114.10
H1	66.00	14.25	17.00	18.72	21.16	22.05	6.24	5.23	4.76	4.21	4.07	158.03	159.21	147.32	116.65	115.13
H2	00.69	14.10	17.00	18.57	21.24	21.95	6.27	5.23	4.77	4.02	4.06	159.32	159.66	149.65	118.32	117.92

Table 3B.3: XRD parameters of EP/Kevlar composites with and with out MA-g-PP:

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Figure 3B.3.b) XRD study of fluorinated Kevlar /EP composite (E), Kevlar /EP/ 2% MA-g-PP composite (E1), Kevlar/ EP/ 5% MA-g-PP (E2)

The enhancement of the crystalline properties is more prominent in case of MA-g-PP compatibilzed oxy-fluorinated Kevlar /EP composites (H1, H2). This can be ascribed as the graft copolymerization at the fiber/matrix interface due to the generation of the peroxy radical (RO_2^*) on the Kevlar surface and the reactive group on that of the matrix resulting better adhesion between the fiber and the matrix.



Figure 3B.3.c) XRD study of oxy-fluorinated Kevlar /EP composite (H), oxyfluorinated Kevlar /EP/ 2% MA-g-PP composite (H1), oxy-fluorinated Kevlar/ EP/ 5% MA-g-PP (H2)

However, MA-g-PP content does not affect the crystallinity of the composites appreciably. It is also note worthy that interplanar distance corresponding to every peak position decreases in case of compatibilized unmodified and modified Kevlar /EP composites which again supports the nucleating ability of MA-g-PP into Kevlar /EP systems and the results obtained from DSC study.

3B.4. DMTA study:

Figure 3B.4 (a-c) show the variation of storage modulus as a function of temperature of all composites. It is evident from the figure that incorporation of both untreated, fluorinated and oxy-fluorinated Kevlar fiber leads to the increase in storage modulus of Kevlar /EP composites. Further enhancement of storage modulus is observed in case of compatibilized unmodified Kevlar /EP fluorinated and oxy-fluorinated Kevlar/EP composites (Figure 3B.4a 3B.4b and 3B.4c).



Figure 3B.4.a) Storage modulus vs. temperature curve of Kevlar /EP composite (B), Kevlar /EP/ 2% MA-g-PP composite (B1), Kevlar/ EP/ 5% MA-g-PP (B2)

This is probably due to the increase in stiffness conferred upon the material by the fibers within the matrix which arises due to the efficient interfacial adhesion between the fibers and the matrix in presence of Ma-g-PP.



Figure 3B.4.b) Storage modulus vs. temperature curve of fluorinated Kevlar /EP composite (E), Kevlar /EP/ 2% MA-g-PP composite (E1), Kevlar/ EP/ 5% MA-g-PP (E2)

The enhancement of the magnitude of storage modulus is much more pronounced in case of oxy-fluorinated Kevlar/EP composite (H1, H2) (Figure 3B.4 c ii, iii) due to the generation of reactive groups (RO_2^*) on the oxy-fluorinated Kevlar surface and on the matrix surface (due to the incorporation of MA-g-PP) resulting stronger interfacial bonding between the fiber and the matrix.



Figure 3B.4.c) Storage modulus vs. temperature curve of oxy-fluorinated Kevlar /EP composite (H), oxy-fluorinated Kevlar /EP/ 2% MA-g-PP composite (H1), oxy-fluorinated Kevlar/ EP/ 5% MA-g-PP (H2)

Storage moduli of the composites increase marginally with an increase in MAg-PP content, indicating enhanced stiffness in case of all composites.

The loss tangent $(\tan \delta)$ of the base polymer and their composites as a function of temperature is shown in Figure 3B.5 (a-c). The loss peaks are indicative of the efficiency of a material to dissipate the mechanical energy.



Figure 3B.5.a) Tan delta vs. temperature curve of Kevlar /EP composite (B), Kevlar /EP/ 2% MA-g-PP composite (B1), Kevlar/ EP/ 5% MA-g-PP (B2)



Figure 3B.5.b) Tan delta vs. temperature curve of fluorinated Kevlar /EP composite (E), Kevlar /EP/ 2% MA-g-PP composite (E1), Kevlar/ EP/ 5% MA-g-PP (E2)

Form these Figures it is clear that tan delta vs. temp curve shows a distinct relaxation peak at around 10° C which is the α -transition of EP polymer. The magnitude of the loss peak is lower in case of all composites in comparison to the neat polymer. Addition of MA-g-PP further lowers the magnitude of loss peak indicating lower mechanical energy dissipation capacity as a result of decreased molecular mobility of the concerned composites giving rise to reduced mechanical loss for both unmodified and fluorinated oxy-fluorinated Kevlar /EP composites (Figure 3B.5a, 3B.5b and 3B.5c).



Figure 3B.5.c) Tan delta vs. temperature curve of oxy-fluorinated Kevlar /EP composite (H), oxy-fluorinated Kevlar /EP/ 2% MA-g-PP composite (H1), oxy-fluorinated Kevlar/ EP/ 5% MA-g-PP (H2)

This is the indication of strong interfacial adhesion between fiber and the matrix in presence MA-g-PP. However the T_g does not shift appreciably with the addition of compatibilizer into the Kevlar /EP system.

3B.5. Flow behavior:

The effect of addition of MA-g-PP on the flow behavior of Kevlar /EP composites is enumerated in Figure 3B.6 (a-c). A comparative account of the variation of viscosity of the virgin matrix (EP) and untreated fluorinated and oxy-fluorinated Kevlar /EP composites have also been included in the same figure to evaluate the effect of surface modification of the fiber as well as the matrix.



Figure 3B.6.a) Viscosity vs. shear rate curve for Kevlar /EP composite (B), Kevlar /EP/ 2% MA-g-PP composite (B1), Kevlar/ EP/ 5% MA-g-PP (B2)

The viscosity of the EP composites increases with the addition of Kevlar fiber into the EP matrix due to the restriction to flow of the matrix provided by the fibers. Viscosity of the treated Kevlar/EP composites increases due to the better fiber/matrix adhesion at the interface which is more prominent in case of oxy-fluorinated Kevlar/EP (H, 3B.6 c i) composites because of the generation of more functional group on the fiber surface resulting better adhesion at the fiber-matrix interface.



Figure 3B.6.b) Viscosity vs. shear rate curve for fluorinated Kevlar /EP composite (E), Kevlar /EP/ 2% MA-g-PP composite (E1), Kevlar/ EP/ 5% MA-g-PP (E2)

From Figure 3B.6 (a-c) it is also observed that the addition of MA-g-PP further increases the viscosity of the composites and this compatibilizing effect is more pronounced in case of oxy-fluorinated Kevlar/EP system (Figure 3B.6 c i ii, ii). The peroxy radicals (RO_2^*) generated on the Kevlar surface may

interact with the anhydride rings of MA-g-PP, thereby forming linkages at the interface. Furthermore, the PP moiety of the MA-g-PP adheres to the long hydrophobic chains of the matrix thus lowering the surface tension of the fibers and forms strong interface which can not be taken place in case of unmodified and fluorinated Kevlar/EP (Figure 3B. 6 a i, ii, iii and Figure 3B.6 b i, ii, iii) composites thus the enhancement of viscosity is not so much for those particular cases. Additionally, the friction between the fiber and the matrix increases which further contributes to the enhancement of viscosity for the treated composites although MA-g-PP content slightly influences the viscosity of the treated composites.



Figure 3B.6.c) Viscosity vs. shear rate curve for i) oxy-fluorinated Kevlar /EP composite (H), oxy-fluorinated Kevlar /EP/ 2% MA-g-PP composite (H1), oxy-fluorinated Kevlar/ EP/ 5% MA-g-PP (H2)

In the high shear rate region, both the treated and untreated composites exhibit approximately same viscosities. Reduction in the interaction between the fibers with extensive alignment along the die entrance results the shear thinning of the polymer melt thereby leading to the flow curves to overlap at high shear rates, which in accordance with the results reported in the literature (178). They have reported a marginal difference in the viscosity of the treated sisal-glass fiber hybrid LLDPE composites at high shear rates.

3B.6. SEM study:

Here the SEM images of the cross-sectional tensile fracture of MA-g-PP compatibilized (2% and 5%) unmodified, fluorinated and oxy-fluorinated Kevlar/ EP composites are illustrated in Figure 3B.7 (a-f).The micrograph clearly indicates a significant difference in the interfacial characteristics of the composites.

It was noticed in our previous work (177) that for untreated composites the fibers appeared to be pulled out from the matrix and for surface treated fiber reinforced Kevlar /EP composites it was evident that fibers were broken down leaving the fibers broken down.

However, the addition of MA-g-PP treated composites (Figure. 7 a-f) displays a fairly better dispersion of the fibers over the continuous EP matrix. The SEM micrographs confirm that coupling agent facilitates direct contact between the fibers and the matrix to a greater extent than the uncompatibilized systems.



Figure 3B.7: SEM photograph of a) unmodified Kevlar/ EP/ 2% MA-g-PP (B1), b) unmodified Kevlar/ EP/ 5% MA-g-PP (B2), c) fluorinated Kevlar / EP/ 2% MA-g-PP (E1), d) fluorinated Kevlar / EP/ 5% MA-g-PP (E2), e) oxy-fluorinated Kevlar / EP/ 2% MA-g-PP (H1), f) oxy-fluorinated Kevlar / EP/ 5% MA-g-PP (H2)

There is a significant reduction in fiber pull outs and barely any gaps between the fibers and the matrix is noticed [Figure 3B.7 (e-f)]. This effect is much more pronounced in case of MA-g-PP compatibilized oxy-fluorinated Kevlar /EP composites resulting best thermal, dynamic mechanical crystalline and rheological properties of that particular composite among all the composites.

Chapter: 3C

Effect of Fluorinated and Oxy-fluorinated Kevlar Fiber Loading on the Properties of EP/Kevlar Composites

Effect of fluorinated and oxy-fluorinated Kevlar fiber loading on the properties of EP/Kevlar composites

Nine samples along with the virgin polymer were prepared to monitor the influence of fluorinated and oxy-fluorinated Kevlar fiber loading on the properties of EP/Kevlar composites. The corresponding formulations are tabulated in Table 3C.1.

Sample Code	EP (%)	Kevlar (%)
EP	100	0
А	100	0.71 (unmodified)
В	100	1.43 (unmodified)
С	100	2.86 (unmodified)
D	100	0.71 (fluorinated)
Е	100	1.43 (fluorinated)
F	100	2.86 (fluorinated)
G	100	0.71 (oxy-fluorinated)
Н	100	1.43 (oxy-fluorinated)
Ι	100	2.86(oxy-fluorinated)

Table 3C.1: Compounding formulation:

3C.1. Preparation of composites:

Ethylene polypropylene in 100% was mixed with three different wt% (0.71%1.43% and 2.86%) of original, fluorinated and oxy-fluorinated Kevlar differently in a Brabender mixer with 60 rpm at 200^oC temperature for 10 min. Then the mixtures were molded in a hydraulic press at 200^oC and at 10 MPa pressure for 10 minutes.

3C.2. FTIR study:

The FTIR spectra of the composite materials along with the pure EP are presented in Figure 1. The peak associated with the primary amine backbone appeared in the cases of C, F, and I, at 3340 cm⁻¹ (173) but in the case of pure EP this peak is not observed, which may be due to the incorporation of Kevlar fiber into the polymer matrix.



Figure 3C.1: FTIR spectra of Pure EP (EP), Kevlar fiber reinforced EP (C), Fluorinated Kevlar fiber reinforced EP (F) and Oxy-fluorinated Kevlar fiber reinforced EP (I)

The peak at 1760 cm⁻¹ in the case of C, F, I showed the characteristic peaks of C=O stretching frequency of Kevlar fiber. The FTIR picture of F and I showed the peaks at 1200 cm⁻¹, which may be the characteristic peak of monofluorinate aliphatic groups (C-F bond), formed due to the fluorination and oxy-fluorination. The figure representing I showed an additional peak at 3400 cm⁻¹ representing OH group due to oxy-fluorination of the Kevlar fiber.

3C.3. Thermal properties:

In order to investigate the effect of Kevlar fiber (unmodified and modified by fluorination and oxy-fluorination) and the fiber loading on thermal stability of the EP matrix, thermo gravimetric (TG) and differential scanning calorimetry (DSC) were carried out. The respective parameters are shown in the Table 3C.2 and the TGA plot of pure EP and EP/Kevlar composites (C, F, I) is shown in Figure 3C.2. In order to avoid any ambiguity, the degradation temperature has been defined as the temperature at which the polymer lost 1% of its weight.

It is observed from Table 3C.2 that heat of fusion is highest for pure EP and then decreases gradually in case of fiber reinforced composites. Heat of fusion is proportional to the crystallinity of the sample, which follows the results of X-ray diffraction. Pure EP shows a melting endotherm, T_m , at about 165°C, and the composites show the values close to the T_m of EP (Table 3C.2). The melting point of EP, however, marginally decreases in case of composites. The depression of the melting temperature of the composites is due to dilution

of the matrix resulting from the incorporation of the filler. With fiber loading, heat of fusion increases for all composites. But in every case the value of heat of fusion is less than that of pure EP.

Sample	1 st decom. Temp. (°C)	2 nd decom. Temp (°C)	$T_m(^{\circ}C)$	$H_{f}(J/g)$
EP	233.0	387.0	165.0	73.0
А	240.0	337.8	161.7	59.6
В	245.0	352.0	162.3	69.2
С	261.8	375.2	162.34	69.6
D	250.0	350.0	162.3	65.6
Е	254.4	352.0	162.4	68.5
F	270.5	379.4	162.9	69.8
G	265.0	379.6	163.3	69.9
Н	269.0	391.0	164.1	70.0
Ι	282.4	413.6	164.6	79.9

Table 3C.2: Thermal parameters of EP, EP/Kevlar composites:

From the Table 3C.2 Figure 3C.2 it is clearly observed that the degradation mainly occurs in two steps for all EP and EP/Kevlar composites. In case of EP, the initial degradation starts at 233°C and continues up to 387°C. The second degradation step starts at 387°C. For EP/Kevlar composite (sample C) the degradation starts at 264°C and continues up to 375°C. However, in case of EP/Kevlar (fluorinated, F) and EP/Kevlar (oxy-fluorinated, I), the initial

degradation starts at a higher temperature (about 270°C, 281.3°C) than C. These TGA results imply that due to incorporation of a functional group into Kevlar fiber, the compatibility of two polymeric species increases leading to higher thermal stability in case of fluorinated and oxy-fluorinated Kevlar fiber/EP composites in comparison to the unmodified Kevlar fiber/EP composites. It is important to point out that incorporation of more functional groups through oxy-fluorination may be the reason for the maximum thermal stability of sample I, because oxy-fluorination generates a controlled amount of long-living RO_2^* radicals. These radicals may be responsible for graft polymerizations leading to the highest thermal stability of I resulting in good compatibility (bonding) between fiber and matrix. Moreover, thermal stability of the Kevlar fiber/EP matrix increases with fiber loading, the effect being more evident in the presence of surface modified fibers. The 1st and 2nd decomposition temperatures of all composites are tabulated in the Table 3. The increment of thermal stability of the composites with fiber loading may be attributed to the incorporation of more fiber giving rise to more adhesion between the fiber and matrix. This increment of thermal stability of the composites with fiber loading may also be due to the incorporation of the high thermal stability aromatic content of Kevlar fiber.



Figure 3C.2: TG study of of Pure EP (EP), Kevlar fiber reinforced EP (C), Fluorinated Kevlar fiber reinforced EP (F) and Oxy-fluorinated Kevlar fiber reinforced EP (I)

3C.4. X-ray study:

X-ray diffraction (XRD) diagram of composites containing 2.86% of fiber (original, fluorinated and oxy fluorinated) are displayed in Figure 3C.3 and the respective parameters are shown in Table 3C.3. From Table 3C.3, it can be seen that the percentage of crystallinity of pure EP decreases with the addition of fiber into the polymer matrix.

				Pea	ak ar	gle		In	terpl	aner		Crystallite Size (A°)					
		ity		(20	in de	egree	e)	Dis	tance	e							
	code	% Crystallin								(A ^o))						
	Sample		$\boldsymbol{\theta}_1$	θ_2	θ_3	θ_4	θ_5	d_1	d_2	d_3	d_4	\mathbf{d}_{5}	\mathbf{p}_1	p_2	p ₃	p_4	p5
	EP	74.00	14.20	16.95	18.70	21.30	21.90	6.26	5.25	4.76	4.12	4.18	116.6	164.6	165.3	137.8	137.9
	Α	47.00	13.50	16.30	18.00	21.20	ı	6.26	5.30	4.81	4.12	ı	134.1	135.1	135.2	102.1	
1	В	52.00	14.20	17.00	18.70	21.32	21.88	6.26	5.23	4.76	4.18	4.06	144.70	156.40	145.60	102.30	102.40
(U	54.00	14.20	17.00	18.70	21.25	21.95	6.26	5.24	4.73	4.19	4.06	118.4	163.9	165.3	106.3	117.4
1	D	53.00	14.20	17.00	18.70	21.30	22.00	6.34	5.23	4.70	4.18	4.06	135.4	161.2	156.2	109.1	137.6
	Щ	58.00	14.20	17.05	18.68	21.34	21.95	6.26	5.22	4.77	4.18	4.06	144.70	145.20	146.70	120.30	120.50
I	ц	59.00	14.00	16.80	18.50	21.15	21.80	6.21	5.22	4.68	4.21	4.03	138.9	171.9	232.2	115.2	122.89
(U	58.00	14.20	17.00	18.70	21.30	21.90	6.29	5.28	4.71	4.18	4.03	149.2	165.2	162.1	112.7	119.12
;	Η	60.00	14.10	16.90	18.66	21.20	21.88	6.31	5.23	4.80	4.02	4.08	155.80	156.40	145.50	113.60	114.10
,	Ι	62.00	14.0	16.80	18.40	21.20	21.70	6.14	5.20	4.65	4.02	4.01	164.2	169.9	175.4	121.0	120.41

Table 3C.3: XRD parameters of EP/Kevlar composites:

This can be ascribed as the Kevlar fiber hinders the migration and diffusion of EP molecular chains to the surface of the growing polymer crystal in the composites, resulting in a decrease in the percent crystallinity of the composite. In case of treated Kevlar fiber reinforced EP composite, % crystallinity increases significantly in comparison to untreated derivatives. This is due to the generation of more functional groups onto the surface of Kevlar fiber during fluorination and oxy-fluorination giving rise to more fiber/matrix adhesion facilitating the crystal growth mechanism.



Figure 3C.3: X-ray pattern of Pure EP (EP), Kevlar fiber reinforced EP (C), Fluorinated Kevlar fiber reinforced EP (F) and Oxy-fluorinated Kevlar fiber reinforced EP (I)

It is also important to point out that the crystallite sizes of composites F and I corresponding to all peak angles (2 θ) are higher than composite C, which

suggested the predominant growth phenomena in case of F and I compared to C. The variation of percentage of crystallinity of composites (both modified and unmodified fiber reinforced EP) with wt% of fiber is displayed in the Figure 3C.4. From Figure 3 it is clear that the percentage of crystallinity increases with fiber content in the matrix for both the unmodified and modified fiber reinforced composites.



Figure 3C.4: Variation of % crystallinity with the wt% of unmodified and modified Kevlar fiber in EP/Kevlar composites

This may be due to the nucleating ability of the short fibers. But in all cases the percentage of crystallinty is less than that of the pure EP (Table 2) as pure EP contains an ordered structure.

3C.5. Dynamic Mechanical analysis:

Figure 3C.5a represents the storage modulus E['], for the EP, EP/Kevlar fiber (with 2.86% of unmodified, fluorinated and oxy-fluorinated Kevlar fiber) composites (C, F, I). The storage modulus of the composites decreases with increasing temperature due to the increase in segmental mobility. All Kevlar filled EP composites show higher storage modulus than pure EP. This increment of storage modulus of composites is due to the reinforcement imparted by Kevlar fibers. The storage modulus increases especially in the glassy region in case of oxy-fluorinated Kevlar fiber reinforced EP composites due to the increase in functional groups. It can be explained by the fact that the functional groups affect the surface characteristics of Kevlar fibers, resulting in improved interfacial adhesion between the fibers and matrix, which reduces molecular mobility of EP.



Figure 3C.5 a) Storage modulus vs. Temperature curve of i) Pure EP (EP), ii) 2.86% of unmodified Kevlar/EP (C), iii) 2.86% of fluorinated Kevlar/EP (F) and iv) 2.86% of oxy-fluorinated Kevlar/EP (I).

The storage modulus graphs show a sharp decrease in the temperature range 0 to 10° C, which correlates with the glass transition temperature of EP.



Figure 3C.5.b) Storage modulus of Pure EP (EP), 0.71% of Kevlar fiber reinforced EP (A), 1.43% of Kevlar fiber reinforced EP (B), and 2.86% of Kevlar fiber reinforced EP (C).

Fiber loading leads to the enhancement of the magnitude of storage modulus of every composite due to the proper reinforcement of filler into the matrix (Figure 3C.5b-d).



Figure 3C.5.c: Storage modulus vs. temperature curve of Pure EP (EP), 0.71% of fluorinated Kevlar fiber reinforced EP (D), 1.43% of fluorinated Kevlar fiber reinforced EP (E), and 2.86% of fluorinated Kevlar fiber reinforced EP (F).

The only exception is the composite, A, which contains the lowest amount of unmodified Kevlar fiber, where the storage modulus is less than that of pure EP. The anomalous result shown by A may be due to the agglomeration of unmodified short Kevlar fiber resulting in phase separation.





The tan δ versus temperature curves of (C, F, I) are presented in Figure 3C.6. It is clearly observed in Figure 6 that one relaxation peak appears at around 10^oC, which is the α -transition of the EP polymer. The α -transition shifted to higher temperatures for C, F, I due to the presence of Kevlar fiber in the EP matrix, which tends to decrease the mobility of the matrix chains. The loss peaks were indicative of the efficiency of the material in dissipating mechanical energy. The magnitude of the loss peak is lower in the case of the oxy-fluorinated derivative (I). The lower magnitude of the loss peak indicates lower mechanical energy dissipation capacity. Hence, the molecular mobility of the composites decreases and the mechanical loss is reduced after

incorporation of the oxy-fluorinated Kevlar fibers in the EP matrix. The transition peak progressively broadens. The broadening of the loss peak in the presence of the filler may be due to the matrix-fiber interaction.



Figure 3C.6: Tan delta vs. temperature curve i) Pure EP (EP), ii) 2.86% of unmodified Kevlar/EP (C), iii) 2.86% of fluorinated Kevlar/EP (F) and iv) 2.86% of oxy-fluorinated Kevlar/EP (I).

The matrix polymer in the adjacent portion of the fiber can be in a different state in comparison to the bulk matrix, which can distort the relaxation of the matrix resulting in a broad tan δ peak. Moreover, with fiber loading for all cases (i.e. for unmodified and modified fiber reinforced composites) tan delta decreases gradually. This shows that with fiber loading and as well as surface modification of fibers, appreciable fiber/matrix interaction takes place resulting in the better damping quality of the

composites, though the variation of T_g does not change very much with fiber loading. Variation of glass transition temperature with fiber loading is shown in Figure 3C.7. From this figure, it is clearly seen that the T_g value for A (12.01) decreases slightly in comparison to the pure EP (12.37^oC). This may be due to other mechanisms of dissipation of energy; such as the effects of sliding fiber/fiber that could exceed those produced fiber/matrix interactions which simultaneously take place (179). From Figure 3A.7 it is also observed that T_g values are maximum for the 1.43% of fiber loading. As the fiber loading increases from 1.43% to 2.86%, T_g decreases in all cases.



Figure 3C.7: Variation of glass transition temperature with wt% of Kevlar for i) original Kevlar /EP, ii) fluorinated Kevlar/ EP and iii) oxy-fluorinated Kevlar/ EP

This may be due to the fact that with fiber loading fiber/fiber slippage is the dominating factor over the fiber/matrix interaction, but for all cases containing 2.86% fiber, T_g values are greater than pure matrix and unmodified fiber/matrix derivatives giving rise to better adhesion due to the surface modification of fiber.

3C.6. SEM study:

The dynamic fracture surface of the composites (A, C, F, I), studied using a scanning electron microscope (SEM), is shown in Figure 8. Figure 8a is the micrograph of sample A containing 0.71% of the unmodified Kevlar fiber reinforced EP. From this figure it is clearly seen that matrix is not properly restrained by the fibers, and the fibers are pulled out from the matrix. This type of poor reinforcement of the fiber leads to the lowest storage modulus as well as the lowest thermal stability and crystallinity of this composite. Figure 8b represents the fracture surface of C, from which it is clear that, though the fibers are well dispersed through out the matrix, some of the fibers are pulled out from the surface leaving holes on the surface. As we move to the fracture micrograph of F and I (Figure 8c and d) we can see that fibers are broken rather than pulling out leading to the better adhesion between the filler and the matrix.



Figure 3C.8: a) SEM photograph of A, b) SEM photograph of C, c) SEM photograph of F and d) SEM photograph of I

This better adhesion for F and I is attributed to the surface modification of fibers by fluorination and oxy-fluorination which introduces functional groups to the surface of the fiber resulting in better adhesion between fiber/matrix, which is more pronounced in the case of I. This is in agreement with the high thermal stability, crystallinity and storage modulus of the modified fiber reinforced EP.
Chapter: 4A

Properties of Syndiotactic Polystyrene Composites with Surface Modified short Kevlar Fiber Properties of Syndiotactic Polystyrene Composites with Surface Modified Short Kevlar Fiber

Three samples along with the neat s-PS were prepared to evaluate the effect of fluorinated and oxy-fluorinated short Kevlar fiber reinforcement on the properties of s-PS/Kevlar composites and the corresponding compounding formulations are depicted in the Table 4A.1.

Sample Code	s-PS (%)	Kevlar (%)
В	100	0
Р	100	0.60 (original)
Q	100	0.60 (fluorinated)
R	100	0.60 (oxy-fluorinated)

Table 4A.1: Compounding formulation:

4A.1. Sample preparation:

3.5g of unmodified and modified Kevlar fiber was mixed with 600g of s-PS separately using twin-screw extruder at 300° C having L/D ratio 17 under 10 rpm. Then the mixtures were molded using injection molding at 290° C melting temperature, 60° C mould temperature and at a flow rate of 20 CCM/S in a BOY22D having L/D ratio 17.5.

4A.2. FTIR study:

The IR spectra of the composite materials along with pure s-PS (B) are represented in Figure 1. The peak associated with primary amine backbone appeared in the cases of P, Q, and R at 3340 cm⁻¹ which is absent in case of pure s-PS. This is due to the incorporation of the Kevlar fiber in to the matrix. The peak at 1760 cm⁻¹ in case of P, Q, R is the characteristic peak of C=O stretching frequency of Kevlar fiber. The FTIR pictures of Q and R show the peak at 1200 cm⁻¹ which are the characteristic peak of monofluorinate aliphatic groups (C-F bond) formed due to the fluorination.



Figure 4A.1: FTIR Study of pure s-PS (B), s-PS/ Kevlar (P), s-PS/fluorinated Kevlar (Q) and s-PS/oxy-fluorinated Kevlar (R)

In addition to that peak, composite R also shows a peak at 3400 cm^{-1} corresponding to the –OH group. This is attributed to the carboxylic acid groups generated at the surface of the Kevlar fiber after oxy-fluorination.

4A.3. Differential Scanning Calometric study (DSC):

The results of the DSC heating scans of the composites are shown in Figure 4A.2 and the corresponding parameters, glass transition temperature (T_g) by both DSC and DMTA, melting temperature (T_m) , crystallization temperature (T_c), heat of fusion (ΔH_f) and percent crystallinty (X_c) are tabulated in Table 4A.2. In order to give the same thermal history all the composites are heated up to 300°C. Figure 4A.2 shows the glass transition temperature of pure s-PS is 100.8°C. On addition of modified and unmodified Kevlar fibers into s-PS slightly affect the T_g of s-PS phase. This shift in T_g to slightly higher side is may be due to the fiber/matrix interaction. This effect is more pronounced in case of composite with oxy-fluorinated Kevlar fibers. This compatibility may be due to the graft copolymers obtained from the free radicals generated in case of oxy-fluorinated derivative. Formation of such products at the interface may enhance the miscibility of the composite R there by affecting the glass transition temperature of the respective component, which exceeds the effect of crystallization. Upon increasing the temperature, the heating curve of s-PS shows an exothermic peak at 148.7°C, which is the crystallization peak of s-PS (180).

Sample	Tg	(⁰ C)	Tc	Tm	ΔH_{f}	$X_{c}(\%)$
Code	By DSC	By DMTA	(^{0}C)	(^{0}C)	(Jg^{-1})	
В	100.8	109.9	140.7	274.4	19.9	38.1
Р	102.7	111.5	148.4	275.3	22.4	42.9
Q	103.8	112.3	148.9	275.8	23.4	44.2
R	104.1	113.8	146.5	274.8	21.0	40.3

 Table 4A.2: Thermal parameters of s-PS/Kevlar composites:

Crystallization peaks shift to the higher temperature side in case of all Kevlar/s-PS composites. This may be due to the nucleating effect of the fibers into the s-PS matrix that supports the increasing crystallization trends in case of all s-PS/Kevlar composites obtained by both DSC and XRD studies. In case of oxy-fluorinated Kevlar fiber reinforced s-PS (composite R), T_c shifts to a little low temperature may be due to the graft copolymerization taken place at the interface of the fiber and matrix leading to the cross linking of the polymers resulting in lower percent crystallinity for this composite.

In this study, the percent of crystallinity of the s-PS/Kevlar composites, normalized for fractional content, increases with addition of Kevlar fiber into the s-PS matrix. This indicates that Kevlar fibers and its modification enhance the nucleation and formation of s-PS crystals. This is another indication of strong interfacial interaction between the components, which modify the crystal perfection and purity. The percentage crystallinity is the maximum in case of fluorinated Kevlar fiber reinforced s-PS, followed by unmodified Kevlar fiber/s-PS and oxy-fluorinated/s-PS composites.



Figure 4A.2: DSC study of pure s-PS (B), s-PS/ Kevlar (P), s-PS/fluorinated Kevlar (Q) and s-PS/oxy-fluorinated Kevlar (R).

This is due to the nucleating ability of the Kevlar fiber. But in case of oxy-fluorinated derivative percent crystallinty decreases appreciably because of the graft polymerization, which leads to the increase in the degree of polymerization resulting to the cross linking and branching at the interface for this composite. Upon further rising of temperature the heating curve of s-PS shows an endotherm at about 274.36^oC, which is the melting endotherm of the neat s-PS. However, the melting temperatures of all s-PS/Kevlar composites don't vary appreciably in comparison to the pure component.

4A.4. Thermal Properties:

In order to see the effect of modified and unmodified Kevlar fiber incorporation on the thermal stability of s-PS, the thermo gravimetric (TG) study was conducted. The TG curves of the composites obtained at a heating rate 10^{0} C/min in air and are shown in Figure 4A.3 and respective parameters are tabulated in Table 4A.3. In order to avoid any ambiguity, the onset degradation temperature has been defined as the temperature at which polymer lost 1% of its weight. From the thermo gram it is observed that degradation starts at higher temperature for all Kevlar/s-PS composites than neat s-PS. This enhancement in onset degradation temperature is more pronounced in case of modified Kevlar/s-PS composites.

Sample	Onset	5%	10%	50%
	Degradation. Temp. (⁰ C)	Degradation Temp (⁰ C)	Degradation Temp (⁰ C)	Degradation Temp (⁰ C)
В	223.8	272.1	280.9	314.2
Р	228.0	288.3	314.5	372.4
Q	241.4	289.7	303.4	351.4
R	249.9	292.4	304.8	350.4

Table 4A.3: Thermal parameters of s-PS/Kevlar composites:



Figure 4A.3: TG Study of pure s-PS (B), s-PS/ Kevlar (P), s-PS/fluorinated Kevlar (Q) and s-PS/oxy-fluorinated Kevlar (R).

This extent of enhancement of thermal stability of the modified Kevlar/s-PS composites is may be due to the incorporation of the functional groups on to the Kevlar surface resulting good compatibility between two polymeric species in case of fluorination and oxy-fluorination. Moreover, it is known that crystalline polymer is thermally more stable than its amorphous counter part due to energy input required overcoming both intermolecular and intermolecular forces. It is important to point out that the extent of more interaction in case of oxy-fluorinated Kevlar/s-PS composites due to more functional groups of oxy-fluorinated Kevlar fiber can be responsible for a

higher thermal stability of the oxy-fluorinated Kevlar fiber reinforced (composite R) composite as oxy-fluorination generates controlled amount of long-living RO_2^* radicals. These radicals further may be responsible for graft polymerizations and crosslinkings leading to the highest thermal stability of R amongst all the composites resulting good adhesion between fiber and the matrix, which exceeds the crystallization effect.

4A.5. X-ray study:

Figure 4A.4 shows the X-ray diffractograms of the pure s-PS and the s-PS/Kevlar composites and the respective parameters are shown in the Table 4A.4. From Figure 4A.4, it is clearly seen that pure s-PS shows only one broad peak at the 2 θ value 20.05⁰ and two very small peaks at 11.75⁰ and 13.35⁰. Upon addition of the modified and unmodified Kevlar fiber in to s-PS matrix, the intensity of the peaks at 2 θ value 11.75⁰ and 13.35⁰ increases. This may be due to the reinforcing ability of the Kevlar fiber in to the s-PS matrix. This increasing intensity of these peaks is more pronounced in case of fluorinated Kevlar fiber reinforced s-PS (Q).

e code	Pea	k ang	le (θ)	Int d	terpla listan (A ⁰)	iner ce	Cry	stallit (A ^o)	e size
Sampl	θ_1	θ_2	θ_3	d_1	\mathbf{d}_2	d_3	\mathbf{p}_1	p_2	p_3
В	11.75	13.35	20.05	7.56	6.66	4.44	I	ı	27.95
Р	11.75	13.55	20.45	7.56	6.56	4.36	206.09	196.22	52.57
Ø	11.7	13.5	20.4	7.59	6.58	4.37	186.75	146.34	48.59
R	12.05	13.65	20.6	7.37	6.51	4.33	116.47	146.65	44.85

Table 4A.4: XRD parameters of s-PS/Kevlar composites



Figure 4A.4: XRD pattern of pure s-PS (B), s-PS/ Kevlar (P), s-PS/fluorinated Kevlar (Q) and s-PS/oxy-fluorinated Kevlar (R).

It is also important to point out that the crystallite sizes of all the Kevlar/s-PS composites corresponds to all peak angles (2θ) are higher than pure s-PS, which suggests that the nucleation and growth is also favored in case of modified and unmodified s-PS/Kevlar composites.

4A.6. Dynamic Mechanical Thermal Analysis (DMTA):

To evaluate the effect of both unmodified and modified fibers on dynamic mechanical properties of s-PS, the storage modulus (\vec{E}) as a function

of temperature is graphically represented in Figure 4A.5. As can be observed, the incorporation of the modified and unmodified fibers gives rise to the considerable increase of the s-PS stiffness. This may be due to the reinforcing nature of the Kevlar fiber. The storage modulus of the composites decreases with increasing temperature because of an increase of segmental mobility of the s-PS. The storage modulus values increases especially in the glassy region for all Kevlar/s-PS composites. This effect is more pronounced in case of oxy-fluorinated Kevlar fiber reinforced s-PS due to more functional groups generated onto the Kevlar surface after the oxy-fluorination of these fibers.



Figure 4A.5: Storage modulus vs. temperature curve of pure s-PS (B), s-PS/ Kevlar (P), s-PS/fluorinated Kevlar (Q) and s-PS/oxy-fluorinated Kevlar (R).

This can be explained by the fact that functional groups affect the surface characteristics of Kevlar fibers resulting in improved adhesion between the fiber and the matrix, which in turn reduces the mobility of the s-PS. The storage modulus graphs show a sharp decrease in the temperature range of 90^{0} C to 100^{0} C, which correlates the glass transition temperature of s-PS.

The loss tangent $(\tan \partial)$, as a function of temperature, of different composites is displayed in Figure 4A.6. The damping properties of the materials give the balance between the elastic phase and viscous phase in a polymeric structure. The damping peaks in the treated composites show a decreased magnitude of $\tan \partial$ in comparison to the virgin s-PS and untreated Kevlar fiber/s-PS composite. This is because the fibers carry a greater extent of stress and allow only a small part of it to strain the interface. Hence, energy dissipation will occur in the polymer matrix and at the interface with a stronger interface characterized by less energy dissipation. Further, in comparison to neat s-PS, the $\tan \partial$ peak of untreated composite exhibit lower magnitude, which in turn shows a higher magnitude with respect to the treated Kevlar fiber/s-PS composites. This envisages that incorporation of the modified Kevlar fiber into the s-PS matrix leads to the better adhesion between the fiber and matrix at the interface.

The temperature corresponding to the peak is normally associated with the glass transition temperature T_g of a polymer. From Figure 4A.6, and Table 4A.3, it is observed that the α -peak of the composites are around 110-115°C, corresponding to that of s-PS. The α -relaxation shifted towards the higher

temperature side in case of composite all composites because of increasing crystallinity. But in case of oxy-fluorinated Kevlar fiber reinforced s-PS (R), the crystallization effect was over shadowed by the grafting mechanism leading to cross linking resulting the better fiber/matrix interaction amongst all the composite materials. The T_g values obtained from the two techniques (DSC and DMTA) are different because of the sensitivity difference between the two methods towards the glass transition temperature and also mentioned in literature (181).



Figure 4A.6: Tan Delta Vs Temperature curve of pure s-PS (B), s-PS/ Kevlar (P), s-PS/fluorinated Kevlar (Q) and s-PS/oxy-fluorinated Kevlar (R).

In addition to the α -relaxation peak, all the composites show another peak at around 122^oC-130^oC, which can be assigned as α' relaxation peak, which is highly pronounced in case of composite Q. This type of relaxation generally occurs in case of highly crystalline polymers between T_g and T_m (melting temperature), therefore it can be assigned to α' relaxation of s-PS. N.G. Sahoo et.al (182) has observed such type of relaxation in the PP/LCP system. This type of relaxation is attributed to the molecular motion of the polymeric materials with in the crystalline phase.

4A.7. SEM study:

The homogeneous dispersion of filler in the polymer matrix is one of the conditions for a composite to show good mechanical strength reinforcement because inhomogeneities can lead to structural defects in the composite material. The dynamic fracture surface of pure s-PS and the composites, studied using a scanning electron microscope (SEM) and the fractograms are shown in Figure 4A.7 (a-d). Figure 4A.7a) shows the fracture surface of the neat sample. Figure 4A.7 b) is the micrograph of the Kevlar fiber reinforced composite (P) where the fibers are randomly oriented and pulled out from the matrix resulting poor adhesion between the fiber and matrix resulting poor thermal as well dynamic mechanical stability of the composite. In case of functionalized Kevlar fiber reinforced composite (by fluorination, Q, Figure 4A.7c), fibers are broken rather pulled out which is the indication of good adhesion between the fiber and the matrix.





Figure 4A.7: a) SEM picture of pure s-PS (B), b) SEM picture of unmodified Kevlar /s-PS (P), c) SEM picture fluorinated Kevlar/s-PS (Q) and d) SEM picture of oxy-fluorinated Kevlar/s-PS (R)

The fractogram of oxy-fluorinated Kevlar fiber reinforced s-PS composite (R) (Figure 4A. 7d) shows that the fiber and the matrix form net work i.e. fibers are well dispersed in the matrix phase giving rise to the best thermo dynamical

and thermal properties as a result of good adhesion between fiber and the matrix.

4A.8. AFM study:

Figure 4A.8- 4A.11 show the two-dimensional and three-dimensional AFM images of neat s-PS (B), s-PS-Kevlar (P), s-PS-fluorinated Kevlar (Q) and s-PS/oxy-fluorinated Kevlar (R) composites. Comparison of the AFM topographies of composites with the surface roughness data, however, suggest that the orientation of the Kevlar fiber during the preparation of composite samples might play more active roles in determining the surface morphology.



Figure 4A.8: a) Two dimensional AFM image of s-PS (B) and b) three dimensional AFM images of s-PS (B)

The maximum surface roughness of B, P, Q and R composites were measured as 30, 46, 98 and 133 nm, respectively. Chen et al (176) showed that the interface roughness could be considered as the index of interface adhesion strength. So, the roughness data of our samples strongly suggested that the adhesion strength of s-PS/oxy-fluorinated Kevlar fiber interface is considerably much higher than of s-PS-fluorinated Kevlar and s-PS- Kevlar composites.



Figure 4A.9: a) Two dimensional AFM image of s-PS/ Kevlar composites (P) and b) Three dimensional AFM image of s-PS/ Kevlar composites (P)



Figure 4A.10 a) Two dimensional AFM image of s-PS/fluorinated Kevlar composite (Q) and b) Three dimensional AFM image of s-PS/fluorinated Kevlar (Q)



Figure 4A.11: a) Two dimensional AFM image of s-PS/oxy-fluorinated Kevlar composite (R) and b) Three dimensional AFM image of s-PS/oxyfluorinated Kevlar composite (R)

This is due to the generation of more functional groups onto the surface of Kevlar fiber during oxy-fluorination, which improved adhesion strength of concerned composite.

Chapter: 4B

Study on the Mechanical Rheological and morphological Properties of Short Kevlar Fiber/s-PS Composites-effect of Oxy-fluorination of Kevlar Study on the Mechanical Rheological and Morphological Properties of Short Kevlar Fiber/s-PS Composites- effect of oxy-fluorination of Kevlar

Two samples along with neat polymer were prepared to evaluate the effect of oxy-fluorinated short Kevlar fiber on the rheological, mechanical properties of the s-PS/ Kevlar composites and the corresponding formulations are tabulated in the Table 4B.1.

Sample Code	s-PS matrix (g)	Kevlar fiber (g)
S	600	0
KS	600	3.5 (untreated)
KSO	600	3.5 (oxy-fluorinated)

 Table 4B.1: Compounding formulation:

4B.1. Preparation of composites:

3.5g of original, and oxy-fluorinated Kevlar fiber was mixed with 600 g of s-PS separately using twin-screw extruder at 300° C having L/D ratio 17 under 10 rpm. Then the mixtures were molded using injection molding at 320° C melting temperature, 60° C mold temperature and at a flow rate of 20 CCM/S in a BOY22D having L/D ratio 17.5.

4B.2. FTIR study:

Figure 4B.1 shows the FTIR results of virgin and modified (oxyfluorinated) Kevlar fibers and the corresponding assignments are tabulated in Table 4B.2. IR spectra of virgin (original) Kevlar (Figure 4B.1.ii) shows three main peaks at ca. 3300 cm⁻¹which is assigned as –NH- stretching frequency, 1650 cm⁻¹ representing the stretching frequency of –C=O- bond) and 1540 cm⁻¹ which is the characteristic peak of -NH- bending frequency (183). There are some additional peaks appeared at ca 1063-1310cm⁻¹ which are the characteristic peak of –C-N, -N-H- and –C-C- vibration (184). The carboxyl/ester groups (C=O) at 1632 cm⁻¹ (which is not very much prominent in the particular case) and the hydroxyl group (O–H) at 3450 cm⁻¹ are observed at the oxy-fluorinated Kevlar fibers (Figure 4B.1.ii).

In addition to this FTIR spectrum of modified Kevlar fiber also shows peaks at ca. 1860 cm⁻¹ representing the acid carbonyl fluoride and 1400 cm⁻¹, which is assigned as mono-fluorinate group.

Wave no. (cm ⁻¹)	Assignments		
Virgin Kevlar			
1) 1650	-C=O stretching		
2) 1540	-NH- bending		
3) 3300	-NH- stretching		
4) 1063	-C-N stretching (primary amine), -NH-, -C-C-vibration		
Oxy-fluorinated Kevlar			
1) 3750-3450	Hydroxyl, -OH		
2) 1860	-C(=O)F (acid carbonyl fluoride)		
3) 1400	-C-F (mono-fluorinate group)		
4) 1632	-C=O (carboxyl ester group)		

Table 4B.2: Assignments of FTIR spectra of Kevlar fiber:



Figure 4B.1: FTIR spectra of i) Kevlar fiber, ii) oxy-fluorinated Kevlar fiber

These results affect the surface characteristics of the fibers, resulting in improved interfacial adhesion between the fibers and the matrix, due to the increase of specific polarity on the oxy-fluorinated carbon fiber surfaces (185, 186).

4B.3. Dynamic Mechanical Thermal Analysis (DMTA):

In Table 4B.3 and Figure 4B.2, course of changes in the conservative (storage) modulus (E') as a function of temperature with vibration frequency of 1 Hz has been shown. From the aforementioned figure it is clearly observed

that with in the elastic deformations (A) for s-PS/Kevlar composites (KS, KSO) along with the neat polymer, oxy-fluorinated Kevlar/ s-PS (KSO) shows highest magnitude of storage modulus followed by the unmodified Kevlar/ s-PS (KS) and neat matrix (S). This is attributed to the reinforcement imparted by the Kevlar fiber into the s-PS matrix. In every composite there is a sharp drop-off in storage modulus (E') in the temperature region $+80^{\circ}$ C to $+100^{\circ}$ C, which correlates with the α -transition (glass transition) region (B) of the s-PS matrix (187).

Sample code	Storage modulus at 25 [°] C (MPa)	Storage modulus at glassy region (MPa)	Tan δ_{max}	T _g (⁰ C)
S	8900	9086	0.73	111.2
KS	9192	8847	0.63	114.3
KSO	9989	9775	0.56	116.0

Table 4B.3: Dynamic mechanical properties of s-PS/Kevlar composites:

Additionally the magnitude of storage modulus (E') of untreated fiber reinforced composite (KS) diminishes after glass region (high viscoelastic deformation region, (C) as compared with the virgin matrix. This anomalous behavior of that particular composite (KS) is imputed to inadequate surface wetting of short fibers with in the s-PS matrix, which conduces to ineffective interface, thereby diminishing the magnitude of storage modulus.



Figure 4B.2: Storage modulus vs. temperature curve of pure s-PS (S), s-PS /unmodified Kevlar (KS), s-PS/ oxy-fluorinated Kevlar (KSO) composites

Conversely, the oxy-fluorinated Kevlar/s-PS composite (KSO) shows a distinct increase in storage modulus (E') in comparison to the virgin polymer (S) in this particular region. This improvement of storage modulus (E') is credited to the change in morphology and also an increase of interaction between the fiber and matrix at the interface due to incorporation of the functional group on to the surface of the Kevlar fiber. Conservative (storage) modulus changes pattern in the elastic transition region (D) is almost same in case of all composites.

Temperature dependency of mechanical loss angle tangent (tan ∂) is presented in Figure 4b.3 and Table 4B.3. It is well known that the energy

damping in viscoelastic polymers originates from inelastic movement of molecular chain segments in the amorphous regions, whereby the applied elastic energy is dissipated as heat. Free volume reaches a critical level in a transition region leading to a high value of damping due to the initiation of molecular motion. Fibers are considered to be elastic in nature while the polymer and the fiber-polymer interface are viscoelastic (188). Hence energy dissipation occurs both in the polymer matrix and at the interface. The stronger interface leads to the less energy dissipation, which is substantiated in the recent experimental results (Figure 4b.3). Figure 4B.3 shows that the tan delta value decreases considerably in case of composites (KS, KSO) in the glass transition region in comparison to the virgin polymer, which is most likely due to the fiber reinforcement that leads to less energy dissipation at the fibermatrix interface. The lowest magnitude of damping peak in case of treated composite gives the information about the existence of fiber-polymer interaction, and at the same time it confirms the effective fiber-matrix interfacial adhesion in case of the particular composite giving rise to the strong interface leading to the lowest energy dissipation at the interface. The α damping peak corresponds to the glass transition temperature (T_{σ}) of the polymer. Glass transition is concerned with a motion caused by diffusion of main chain segments in the non-crystalline regions, under the structural simplicity of molecular chains in the crystalline regions. The glass transition temperature (T_g) of the composites shifts slightly to the higher temperature side in comparison to the neat polymer, which is also the indication of reinforcing nature of fiber in to the s-PS matrix.



Figure 4B.3: Tan delta vs. Temperature curve of pure s-PS (S), s-PS/ unmodified Kevlar (KS), s-PS/ oxy-fluorinated Kevlar (KSO) composites

In case of treated composite (KSO), the peroxy radical (RO_2^*) generated at the surface of the oxy-fluorinated Kevlar fiber leads to the graft co-polymerization at the fiber-matrix interface resulting to the better interfacial adhesion between the fiber and matrix.

4B.4. Rheological properties:

The variation of steady state viscosity (η) as a function of shear rate (γ) is represented in Figure 4B.4. From the figure it is evident that viscosity of the virgin polymer i.e s-PS (S) increases with the addition of Kevlar fiber in the composites (KS). In the case of fiber filled systems, the fibers perturb the normal flow of the polymer and hinder the mobility of the chain segments in

the direction of the flow (189). The effect of oxy-fluorinated Kevlar fiber on the viscosity of the s-PS/ Kevlar composite (KSO) is also enumerated in figure 4B.4.

It is observed from the figure that viscosity of KSO further increases in comparison to the unmodified Kevlar/s-PS (KS) composite. Introduction of reactive functional groups on the surface of the Kevlar fiber increases the surface polarity of the fibers resulting the formation interfacial bonds between the fiber and matrix through the ester linkages, which in turn lowers the surface tension of the fibers. Additionally, the friction between the fiber and the matrix is also increased which leads to the further enhancement of the viscosity of the treated composites (KSO).



Figure 4B.4: Viscosity vs. shear rate curve of pure s-PS (S), s-PS /unmodified Kevlar (KS), s-PS/ oxy-fluorinated Kevlar (KSO) composites

It is interesting to point out that in every fiber reinforced composites as well as the virgin polymer, the curves reveal the typical pseudo plastic nature, showing a decrease in viscosity with shear rates. At low shear rates the fibers displayed larger reinforcing capabilities, which is mainly attributed to the fiber-fiber interactions arising from weak structures made up by agglomerates of non-aligned fibers (190). In the high range of shear rates, shear-thinning behavior of the composite melt persisted and all the composites show nearly the same viscosity. This can be attributed to the alignment of the fibers at high shear rates along the major axis thereby decreasing the fiber-fiber collision. However, the enhancement of viscosity at this temperature is attributed to the fine dispersion of the fibers into the matrix resulting from the oxy-fluorination of the Kevlar fiber.

4B.5. Mechanical properties:

The values of elastic modulus, tensile strength and elongation at break along with their deviations are listed in Table 4B.4. A decreasing trend of elastic modulus, tensile strength and elongation at break with the incorporation of the untreated fiber into the virgin matrix is observed (KS). This detrimental effect of Kevlar fibers on the mechanical properties of the resulting composite is a demarcation with the results reported in literature, for Kevlar fiber reinforced polymers (4). It may be due to the weak fiber-matrix interface derived from the divergent behavior in polarity between the hydrophilic Kevlar fibers and the hydrophobic s-PS matrix. Raj et.al (191) reported the same observation in the high impact polystyrene and sisal fiber system. Surface treatment of Kevlar fiber by oxy-fluorination improves the mechanical properties of the treated composite (KSO) well appreciably.

Sample	Tensile	Elastic	Elongation at	Impact
code	Strength	modulus	break (%)	Strength
	(MPa)	(MPa)		(kJ/m^2)
S	48.08	3473	1.4	6.6
KS	46.87	3310	1.26	6.25
KSO	52.23	3559	1.51	7.45

 Table 4B.4: Mechanical properties of s-PS/Kevlar composites:

From table 4B.4 it is clear that tensile strength increases about 12% in case of treated composite (KSO) in comparison to the untreated one (KS). Similarly, the magnitude of elongation at break (19%) and elastic modulus also increases in case of treated composite. This probably due to the improved bond strength between the fiber and matrix at interface arising from the oxy-fluorination of Kevlar fiber which contributes to the efficient stress transfer from the matrix to the fiber.

Impact strength of the composite (KS) decreases with the addition of the fiber (Table 5) indicating the immobilization of the matrix molecular chain by the fibers. This leads to the increased stress concentration by limiting the composite's ability to adapt the deformation, which makes the concerned composite more brittle. This can be attributed as the weak fiber/matrix interaction at the interface. Oxy-fluorinated Kevlar/s-PS composite (KSO)

b

exhibits an appreciable enhanced magnitude of impact strength (at about 19.25%) in comparison to the untreated composite confirming the better fiber/matrix interaction at the interface.

4B.6. Scanning Electron Microscopy:

а

The mechanical findings can be further underpinned with the morphological evidences. The SEM micrographs of the tensile fractured surfaces of untreated and treated composites are depicted in figures 4B.5 (a-b).

The micrographs clearly indicate a significant difference in the interfacial characteristics of the composites.



Figure 4B.5: SEM Picture of (a) unmodified Kevlar / s-PS (KS) (b) oxyfluorinated Kevlar / s-PS (KSO)

In case of untreated fiber reinforced composite figure 5a the fibers appears to be free from the matrix material and a large number of fiber pullouts are noticed. This indicates poor interfacial adhesion between the fibers and the matrix n case of untreated composite. This is attributed to the fact of increasing fluorine/oxygen functional groups on Kevlar fiber surfaces, resulting in the van der waals interaction (192) with the fiber and the matrix at the interface-giving rise to effective stress transfer between the fiber and matrix resulting superior mechanical, dynamic properties for that particular composite.

Chapter: 5

Simulation of the Fiber Orientation of Kevlar in s-PS/Kevlar Composites-effect of Fluorinated and Oxy-fluorinated Kevlar Fiber on the Properties and Processibility Simulation of the Fiber Orientation of Kevlar in s-PS/ Kevlar Composites- effect of fluorinated and oxyfluorinated Kevlar Fiber on the Properties and Processibility

Sixteen samples along with various injection molding conditions were prepared to appraise the effect of processing parameters on the various physico-chemical properties and the simulation of fiber orientation of the fluorinated and oxy-fluorinated short Kevlar fiber reinforced s-PS by mold flow technique. The compounding formulations are depicted in the Table 5.1.

Sample Code	s-PS (g)	Kevlar (g)
Series I	600	0
Series II	600	3.5 (original)
Series III	600	3.5 (fluorinated)
Series IV	600	3.5 (oxy-fluorinated)

Table 5.1: Compounding formulations:

5.1. Preparation of composites:

600g of SPS was mixed with 3.5g of original, and fluorinated Kevlar fiber differently in a twin screw extruder having L/D ratio 17 under 10 r.p.m. The compounding formulation is given in table 1. Then the melt blended materials were injection molded by BOY22D machine having L/D ratio 17.5 under the different condition as tabulated in Table 5.2.

Sample Code	$T_m (^0C)$	T_{mold} (⁰ C)	Flow rate (cm ³ /s)
Series IA/ Series IIA/ Series IIIA/IVA	290	60	20
Series IB/ Series IIB Series IIIB/IVB	290	60	48
Series IC/ Series IIC Series IIIC/IVC	320	40	20
Series ID/ Series IID Series IIID/IVD	320	60	20

Table 5.2: Processing parameters for injection molding:

5.2. Differential Scanning Calorimetric Study (DSC):

The results of the DSC heating scans of the Kevlar/ s-PS composites under different molding conditions are illustrated in Figure 5.1(a-d) and the corresponding parameters, glass transition temperatures (T_g), melting temperatures (T_m), crystallization temperature (T_c), heat of fusion (ΔH_f) and percent crystallinity are tabulated in Table 5.3. All the composites are heated up to 300^oC to maintain the same thermal history. Here we have discussed the effect of melt temperature (keeping mold temperature and flow rate constant), mold temperature (where melt temperature and flow rate remain constant) and flow rate (melt and mold temperature remain unchanged) on the thermal properties of the unmodified and modified Kevlar fiber reinforced s-PS composites.

Effect of flow rate

The injection flow rate parameter is very significant so that it can be changes very rapidly and in turn it can change the thermal as well as the crystalline properties of the final product very dramatically. Figure 5.1(a-d) and Table 5.3 show the variation of the crystalline and thermal properties of the s-PS and s-PS/Kevlar composites along the flow direction of the polymer melts. There are many contradicting reports are available to state the influence of injection flow rate on the crystallinity of the polymer materials. C. M. Hsuing et.al (193) reported that lower injection speed results in enhanced crystallinity in polymer melt at lower injection mold temperature and at higher temperature, where the thermally activated crystallization is dominant; the effect of injection speed is minimal. The same author again reported an opposite view (194). They have accounted that at a particular mold temperature, the high speed resulted in slightly higher crystallinity. Our observation is in line with that of the latter case i.e. crystallinity increases very significantly with the rise in flow rate of the injection molding [Series IA, IB] (Figure 5.1a); IIA, IIB (Figure 5.1b); IIIA, IIIB (Figure 5.1c) and IVA, IVB (Figure 5.1d)]. This may be ascribed as the rapid filling of the mold cavity keeps the polymer melt at high temperatures for longer time thus the level of crystallinity of the materials increases (195). However, reinforced composites show higher crystallinity in comparison to the virgin polymer because of the nucleating effect of the fibers. Again modified fibers show further increased crystallinity as a result of better fiber-matrix interaction at the interface due to
the introduction of the functional groups on to the Kevlar surface. The crystallization temperature shifts towards the higher temperature side

Sample Code	Tg (⁰ C)	Tc (⁰ C)	Tm (⁰ C)	$\Delta H_{f} (Jg^{-1})$	X _c (%)
IA	100.8	140 7	274 4	199	38.1
IB	101.5	148.0	276.0	21.9	41.2
IC	101.3	273.9	147.8	16.9	31.8
ID	101.0	147.6	273.5	17.9	33.6
IIA	102.7	148.4	275.3	22.4	42.9
IIB	103.2	153.0	274.8	23.9	44.9
IIC	102.7	151.9	276.8	21.0	39.5
IID	102.0	152.0	275.3	22.2	41.7
IIIA	103.8	148.9	275.8	23.4	44.2
IIIB	104.0	150.3	277.8	24.0	45.2
IIIC	103.5	149.8	277.8	21.5	40.4
IIID	103.3	149.7	276.8	23.2	43.6
IVA	104.1	274.8	146.5	21.0	40.3
IVB	105.0	275.2	147.3	22.9	43.0
IVC	103.9	274.5	146.8	22.4	42.1
IVD	104.4	275.3	147.4	22.8	42.9

 Table 5.3: Thermal parameters of s-PS/Kevlar composites under different processing parameters:

supporting the enhanced crystallization trend of the composites under this particular processing parameter. Glass transition temperature (T_g) of the composites along with the neat polymer also exhibits the increasing trend, which also corroborates with the enhanced crystallinity of the concerned polymer materials.

However, there is an optimized condition under which the thermal and crystalline properties of all polymer materials possess maximum value (Series IB, IIB, IIIB and IVB).



Figure 5.1.a: DSC study of pure s-PS under different processing parameters A, B, C and D



Figure 5.1b: DSC study of unmodified Kevlar/s-PS composites under different processing parameters (A, B, C and D)

Effect of mold temperature

Mold temperature has strong influence on the crystalline as well thermal properties of the polymer materials as reported by many researchers (193-194, 196-197). In our study we have seen a distinct effect of mold temperature on the properties of Kevlar/s-PS composites. Form DSC outline (Figure 5.1 (a-d) and the corresponding Table (Table 5.3), it is apparent that with rise of mold temperature, crystallinity of the composites along with the neat polymer [Series IC, ID (Figure 5.1a); Series IIC, IID (Figure 5.1b); Series IIIC, IIID (Figure 5.1c) and Series IVC, Series IVD (Figure 5.1d)] varies appreciably to an enhanced magnitude. This may be manifested as the reduction of cooling rate at higher molding temperature leading to the generation of crystallites in the polymer materials resulting freezing in more free volume (193, 198). The Same observation was reported by K. Banik et.al, C. M. Hsiung et.al (197, 195). The DSC results also exhibit the higher glass transition temperature for the composites and pure polymer processed at higher mold temperature (Figure 1a, b and c and Table III), which may be indeed an indication of more constraints to the amorphous phase exerted by the increased crystallinty. This enhancement is further more prominent in case of modified Kevlar/s-PS composites, as a result of more fiber/matrix adhesion.



Figure 5.1c: DSC study of fluorinated Kevlar/s-PS composites under different processing parameters (A, B, C and D)

Crystallization temperature also shifted towards higher temperature side, which again supports the trends of increased crystallinty of the materials.

Effect of melt temperature

From the Figure 5.1a, b, c, d and Table 3, it is quite clear that with addition of unmodified as well as modified Kevlar into the s-PS matrix results in enhancement of the crystallinity of the composites in comparison to the neat polymer because fiber can act as the nucleation sites for crystalline growth of the polymer matrix. This enhancement is very much pronounced in case of fluorinated Kevlar/s-PS composites as a result of introduction of functional

groups on to the Kevlar surface resulting better fiber/matrix interaction at the interface (178, 199). From the DSC profile of the composites [Series IA, IIA, IIIA, IVA (Figure 5.1a, b, c, d) and Series ID, IID and IIID, IVD (Figure 5.1a, b, c, d)] it is clearly evident that melting temperature does not influence the crystalline properties as well as the thermal behavior of the composites.



Figure 5.1d: DSC study of oxy-fluorinated Kevlar/s-PS composites under different processing parameters (A, B, C and D)

Though somewhat very low diminution of the crystallinity in case of unmodified and modified composites has been observed at higher melt temperature this is in line with the observation of P. Singh et.al (22). But in case of oxy-fluorinated derivative the reverse trend has been observed. The crystallization peak shifted towards higher temperature side in case of reinforced polymer in comparison to the neat one. This may be again due to the nucleation effect imparted by the fibers into the matrix. However, glass transition temperature of all composites along with the virgin polymer shift towards lower temperature region very marginally.

5.3. X-ray study:

Figure 5.2 (a-d) presents the X-ray diffractograms of s-PS and the unmodified and modified Kevlar/s-PS composites under varying processing parameters and the corresponding results are depicted in Table 5.4. From Figure 5.2a and Table 5.4, it is clearly evident that s-PS possesses one broad peak near about $2\theta = 20.08$ and two small peaks c.a. $2\theta = 11.75^{\circ}$ and 13.35° under different processing condition (IA, IB, IC and ID) (199). Incorporation of unmodified and modified Kevlar fiber into the s-PS matrix significantly enhances the peak intensity of all composites under all processing parameters (Figure 2a, b, c and d and Table 4). This can be ascribed as the nucleating ability of the fibers into the s-PS matrix, which is in line with the results observed from DSC.



Figure 5.2a: XRD pattern of pure s-PS under different processing parameters (A, B, C and D)

With rise in flow rate the diffractograms of every composite along with the neat polymer [Series IA, IB (Figure 5.2a); IIA, IIB (Figure 5.2b); IIIA, IIIB (Figure 5.2c); and IVA, IVB (Figure 5.2d)] appear to be more intense for all crystalline peaks.

Higher crystallite size corresponding to all peak position also favors nucleation and growth mechanism in case of those particular composites under specific processing condition possessing higher crystalline properties, which again supports the results obtained from DSC.

ole e	linity	Ре	Peak angle (20)		l di	Interplaner distance (A ⁰)		crystallite size (A ⁰)		
Sam cod	Crystal	θ_1	θ_2	θ_3	d ₁	d ₂	d ₃	p_1	p ₂	p ₃
IA	30.1	11.7	13.3	20.0	7.56	6.66	4.44			7.95
B	33.7	11.93	13.69	20.68	7.44	6.49	4.31	206.1	196.2	29.0
IC	27.2	11.87	13.48	20.34	7.48	6.59	4.38			19.81
Ð	28.0	11.93	13.61	20.40	7.44	6.53	4.37	1		19.84
IIA	34.6	11.75	13.55	20.45	7.56	6.56	4.36	206.09	196.22	52.57
IIB	36.7	12.00	13.88	20.74	7.40	6.40	4.30	210.23	200.01	54.06
IIC	31.9	12.00	13.53	20.40	7.40	6.57	4.37	117.07	92.88	52.57
Ð	33.3	12.00	13.51	20.41	7.40	6.58	4.36	130.2	154.8	92.88
IIIA	36.5	11.7	13.5	20.4	7.59	6.58	4.37	186.75	146.34	48.59
IIIB	38.6	11.90	13.60	20.65	7.47	6.55	4.32	187.12	160.67	66.72
IIIC	32.7	11.75	13.82	20.41	7.56	6.43	4.37	136.58	119.07	49.40
Ð	34.0	11.80	13.55	20.44	7.53	6.61	4.36	165.85	165.85	0 10
IVA	32.4	12.05	13.65	20.6	7.37	6.51	4.33	116.47	146.65	44.85
IVB	35.5	12.2	13.6	20.6	7.27	6.50	4.32	118.3	160.5	63.61
IVC	32.1	11.85	13.54	20.52	7.50	6.62	4.34	112.0	109.3	43.94
IVD	32.9	11.55	13.53	20.31	69.7	6.61	4.39	116.8	150.9	57.03

Table 5.4: X-ray parameters of s-PS/Kevlar composites under different processing parameters

Mold temperature significantly affects the x-ray diffraction pattern of all composites along with the neat polymer (Figure 5.2a-d) and Table 5.4). Composites processed at higher mold temperature (ID, IID, IIID and IVD) possess more intense peaks and higher crystallite sizes and lower interplaner spacing indicating better crystalline properties for that particular case in comparison to the lower derivative (IC, IIC, IIIC and IVC) (Figure 5.2a, b, c, d). These enhanced crystallinity trends at higher mold temperature supports the results obtained from DSC study.



Figure 5.2b: XRD pattern of unmodified Kevlar/s-PS composites under different processing parameters (A, B, C and D)

Higher melt temperature (Series ID, IID, IIID and IVD) results slightly diminishing peak intensity, higher interspacing distance and lower crystallite size corresponding to each peak (Figure 5.2(a-d) and Table 5.4) than that of lower case (Series IA, IIA, IIIA and IVA) (Figure 5.2 a, b, c, d) supporting the

results prevailed from DSC. For oxy-fluorinated derivative somewhat reverse trend has been observed (Figure 5.4d and Table 5.4).



Figure 5.2c: XRD pattern of fluorinated Kevlar/s-PS composites under different processing parameters (A, B, C and D)



Figure 5.2d: XRD pattern of oxy-fluorinated Kevlar/s-PS composites under different processing parameters (A, B, C and D)

This again corroborates the results obtained from DSC.

5.4. Simulation of fiber orientation by mold flow technique:

In our study we have dealt with s-PS/Kevlar composites and the effect of fluorination and oxy-fluorination on the fiber orientation of that particular composite under varying processing condition. The variation of orientation tensor (T_{xx}) with normalized thickness for the unmodified and modified s-PS/Kevlar composites under varying processing conditions are displayed in the Figure 5.3 (a-c) and the orientation pattern of the same in the three different normalized thick ness are displayed in Figure 5.4 (a-c). From those figures 5.3 (a-c) and 5.4 (a-c), it is clear that processing parameters has a significant effect on the orientation of fibers in the composites along with the pure materials used along the flow direction. Moreover, the fiber orientation is different in skin and core region in case of different composites.



Figure5.3a: Fiber orientation tensor vs. normalized thickness of unmodified Kevlar/s-PS under different processing parameters (A, B, C and D).

The variation of orientation tensor as a function of normalized thickness is represented in Figure 5.3 (a-c) under various processing conditions and the fiber orientation at the skin and core region for every composites under varying processing parameters are depicted in Figure 5.4 (a-d), 5.5 (a-d) and 5.6 (a-d).



Figure 5.3b: Fiber orientation tensor vs. normalized thickness of fluorinated Kevlar/ s-PS under different processing parameters (A, B, C and D).



Figure 5.3c: Fiber orientation tensor vs. normalized thickness of fluorinated Kevlar/s-PS under different processing parameters (A, B, C and D).

At lower flow rate the fibers are more oriented in the core region than in the skin in case both unmodified and modified fiber reinforced composites [Series IIA, IIIA and IVA as evidenced from Figure 5.3 (a-c) and 5.4a. i, ii, iii, 5.5b i, ii, iii and 5.6c i, ii, iii]. But in case of higher flow rate the reverse trend has been observed i.e. the magnitude of the fiber orientation tensor (T_{xx}) is greater in the skin region than that of core region for all composites [Series IIB, IIIB, and IVB] Figure 5.3(a-c), 5.4b i, ii, iii, 5.5b i, ii, iii and 5.6b i, ii, iii, which is in line with the observation of Bright et.al (200).





Figure 5.4a: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.965709), ii) core region (normalized thickness= 0, T_{xx} = 0.968493), iii) top surface (normalized thickness = 1, T_{xx} = 0.965709) of unmodified Kevlar /s-PS composites (Series IIA).

This can be ascribed as in the core region molding shearing flow is predominant and at higher flow rate the fibers flow almost with out shearing thus orienting the fibers in the transverse to the flow direction in the concerned region. But in case of skin region the shear rate aligns more fibers in the flow direction resulting to the higher orientation tensor value.



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Figure 5.4b: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.972762), ii) core region (normalized thickness= 0, T_{xx} =0.957614), iii) top surface (normalized thickness = 1, T_{xx} = 0.972762) of fluorinated Kevlar /s-PS composites (Series IIB).

An interesting trend of fiber orientation has been observed in case of varying mold temperature (Series IIC, IID, Figure 5.3 a, 5.4 c i, ii, iii, 5.4d i, ii, iii; IIIC, IIID, Figure 5.3b, 5.5c i, ii, iii, 5.5d i, ii, iii; and IVC, IVD Figure 5.3c, Figure and 5.6 c i, ii, iii, 5.6d i, ii, iii). At higher mold temperature more fibers are oriented in core region than that of the skin (greater orientation tensor value) and in case of lower mold temperature the opposite trend has been observed



Figure 5.4c: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.972678), ii) core region (normalized thickness= 0, T_{xx} = 0.956036), iii) top surface (normalized thickness = 1, T_{xx} = 0.972678) of fluorinated Kevlar /s-PS composites (Series IIC).

For high mold temperature, the temperature difference between the molten fluid and mold temperature leads to the thinner solidified skin leading to the lower flow field at the solid-melt interface and lower shear rates in the solid-melt interface thus orienting lesser fiber in the flow direction in this concerned region.



Figure 5.4d: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.96074), ii) core region (normalized thickness= 0, T_{xx} = 0.966417), iii) top surface (normalized thickness = 1, T_{xx} = 0.96074) of fluorinated Kevlar /s-PS composites (Series IID).



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Figure 5.5a: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.952928), ii) core region (normalized thickness= 0, T_{xx} = 0.966434), iii) top surface (normalized thickness = 1, T_{xx} = 0.952928) of fluorinated Kevlar /s-PS composites (Series IIIA).





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Figure 5.5b: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.963298), ii) core region (normalized thickness= 0, T_{xx} = 0.956258), iii) top surface (normalized thickness = 1, T_{xx} = 0.963298) of fluorinated Kevlar /s-PS composites (Series IIIB).

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Figure 5.5c: Fiber orientation at the i) bottom surface (normalized thickness= - 1, T_{xx} = 0.964488), ii) core region (normalized thickness= 0, T_{xx} = 0.956879), iii) top surface (normalized thickness = 1, T_{xx} =0.964488) of fluorinated Kevlar /s-PS composites (Series IIIC)

However, melt temperature has also a pronounced effect on the fiber orientation as evidenced from Figure 5.3 (a-d) and 5.4a i, ii, iii, d i, ii, iii; 5.5a i, ii, iii, d i, ii, iii; and 5.6a i, ii, iii, d i, ii, iii. Although the T_{xx} shows the similar trend in the core as well as in skin region at both higher and lower melt

temperature (Series IIA, 5.3a, 5.4a i, ii, iii, IID, 5.3a,; IIIA, IIID; and IVA, IVD). The fibers are more oriented in the core region (higher magnitude of orientation tensor) than that of the skin. However, higher melt temperature possess some what less fiber orientation tensor than that of the lower variable.



Figure 5.5d: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.952551), ii) core region (normalized thickness= 0, T_{xx} = 0.965979), iii) top surface (normalized thickness = 1, T_{xx} =0.952551) of fluorinated Kevlar /s-PS composites (Series IIID)

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Figure 5.5a: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.966716), ii) core region (normalized thickness= 0, T_{xx} = 0.968575), iii) top surface (normalized thickness = 1, T_{xx} = 0.966716) of oxy-fluorinated Kevlar /s-PS composites (Series IVA)

However, MOLDFLOW does not consider fiber/matrix adhesion in their program. As mentioned earlier that it uses the Folgar-Tucker model, which is a modification of the Jeffery model by adding a diffusive term to consider the fiber-fiber interaction. In the Jeffery model, inertia and Brownian motion of the fibers are neglected.



Figure 5.5b: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.96284), ii) core region (normalized thickness= 0, T_{xx} = 0.960886), iii) top surface (normalized thickness = 1, T_{xx} = 0.96284) of oxy-fluorinated Kevlar /s-PS composites (Series IVB)

The fibers the Jeffery model considers are rigid particles moving in a Newtonian fluid, which - however - do not disturb the motion of the fluid. So it is not important whether the fiber/matrix adhesion is good or not in mold flow technique.



Figure 5.5c: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.967202), ii) core region (normalized thickness= 0, T_{xx} = 0.966912), iii) top surface (normalized thickness = 1, T_{xx} =0.96284) of oxy-fluorinated Kevlar /s-PS composites (Series IVC)

It is also note worthy that although MOLD FLOW does not consider the fiber/matrix adhesion; the orientation tensor value is the maximum in case of series IIB and IIIB, both in the skin as well as in the core region manifesting the most fiber orientation in the flow direction, which is the optimum condition for the crystalline and thermal properties of the composites corroborating the results obtained from DSC and XRD (Figure 3a and b).



Figure 5.5d: Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.965483), ii) core region (normalized thickness= 0, T_{xx} = 0.96677), iii) top surface (normalized thickness = 1, T_{xx} = 0.965483) of oxy-fluorinated Kevlar /s-PS composites (Series IVD)

5.52 SEM study:

To understand the fiber/matrix adhesion in the unmodified and modified Kevlar/s-PS composites, SEM study of the dynamic fractured surface was carried out only for IB, IIB and IIIB and the fractograms are shown in Figure 5.6 (a-d).



Figure 5.6: a) SEM picture of cryfractured surface of pure s-PS under processing condition B, b) SEM picture of cryfractured surface of unmodified Kevlar/s-PS under processing condition B, c) SEM picture of cryfractured surface of fluorinated Kevlar/s-PS under processing condition B, and d) SEM picture of cryfractured surface of oxy-fluorinated Kevlar/s-PS under processing condition B

From the Figure 5.6b, it is quite evidenced that incase of IIB fibers are pulled out and not uniformly distributed in the matrix. In case of IIIB (Figure 5.6c) fibers are broken down rather pulled out from the matrix and more uniformly distributed through out the matrix indicating better fiber /matrix interaction at the interface and for IVB (Figure 5.6d) fibers are not only broken down from the matrix also are covered by the matrix , which is responsible for the better crystalline and thermal properties of the modified Kevlar reinforced s-PS composites due to the generation of the functional groups onto the Kevlar surface (199).

Chapter: 6

Effect of Fluorinated and Oxy-fluorinated Short Kevlar Fiber Reinforcement on the Properties of PC/LCP Blends Effect of fluorinated and oxy-fluorinated short Kevlar fiber reinforcement on the properties of PC/LCP blends

Four samples along with the neat polymer were prepared to evaluate the effect of fluorinated and oxy-fluorinated short Kevlar fiber reinforcement on the properties of PC/LCP hybrid composites and the corresponding compounding formulations are depicted in the Table 6.1:

Sample code	PC (%)	LCP (%)	Kevlar (%)
PC	100	-	-
Н	100	20.8	-
Ι	100	20.8	0.5 (original)
J	100	20.8	0.5 (fluorinated)
K	100	20.8	0.5 (oxy-fluorinated)

 Table 6.1: compounding formulations:

6.1. Preparation of blends:

0.5 weight% of original, fluorinated and oxy-fluorinated Kevlar fiber was mixed with a mixture containing 100 weight% of PC and 20.8 weight% of LCP blend using a twin-screw extruder at 320^oC having L/D ratio 17 under 20 rpm. Then the mixtures were molded using injection molding at 320^oC melting temperature, 40^oC mold temperature and at a flow rate of 48 CCM/S in a BOY22D having L/D ratio 17.5.

6.2. Differential Scanning Calorimatric study (DSC):

The DSC heating profile of PC/LCP and unmodified and modified Kevlar composites along with the neat polymer (in the temperature range 80° - 200° C) is depicted in Figure 6.1 and the magnitude of glass transition temperature of the concerned blends are tabulated in Table 6.2. Figure shows only one transition in the range of 150°C for pure PC, which correlates with the glass transition temperature of poly carbonate (198). With addition of LCP the $T_{\rm g}$ shifted to the lower temperature side along with an additional peak near about 135°C (199), which is the glass transition temperature of LCP in the PC/LCP blend as evidenced from the Figure 6.1. The double humped peak arises due to the partial miscibility of the PC with LCP phase i.e. the synergistic effect PC and LCP in the resulting blend. The shifting of the glass transition temperature of PC phase towards the lower temperature side may be ascribed as three contributing factors: the partial miscibility of LCP with the PC matrix i.e. amorphous part of the LCP is miscible with amorphous PC phase, the decrease in the T_g of PC may be caused by the plasticization effect of low molecular weight fraction of the LCP and lastly the decrease in the Tg of PC is attributed to the surface effect i.e. addition of LCP into PC increases the surface area (per unit volume) of the polycarbonate as polycarbonate molecules at the interface region have higher mobility than those in the bulk due to less constraint, in turn increased surface area should decrease the $T_{\rm g}$ of Polycarbonate (198).



Figure 6.1: DSC profile of Pure PC (PC), PC/LCP (H), PC/LCP/ unmodified Kevlar (I), PC/LCP/ fluorinated Kevlar and PC/LCP/oxy-fluorinated Kevlar

With addition of unmodified Kevlar fiber the DSC profile again exhibits a single T_g indicating the miscibility of the PC/LCP in presence of Kevlar fiber, although the magnitude of the T_g of PC matrix shifted towards the lower temperature side may be due to the poor fiber/matrix adhesion at the interface. Fluorination and oxy-fluorination of Kevlar fiber further shift the T_g of the aforementioned blends to the higher temperature side due to the better fiber/matrix adhesion at the interface as a result of incorporation of reactive functional groups onto the Kevlar surface, which is the synergistic effect between the PC/LCP and modified Kevlar. The shifting of T_g towards the higher temperature side is much more prominent in case of oxy-fluorinated derivative.

6.3. Thermal properties:

In order to monitor the effect of modified and unmodified Kevlar fiber incorporation on the thermal stability of PC/LCP blends along with the LCP incorporation, the thermo gravimetric (TG) study was conducted. The TG curves of the composites obtained at a heating rate 10^oC/min in air and are shown in Figure 6.2 and the respective parameters are tabulated in Table 6.2. In order to avoid any ambiguity, the onset degradation temperature has been defined as the temperature at which polymer lost 1% of its weight. From the thermo gram it is observed that degradation starts at higher temperature for all Kevlar/PC/LCP blends than neat PC and PC/LCP. This enhancement in onset degradation temperature is more pronounced in case of modified Kevlar/PC/LCP composites.

Sample	Degradation	Mass	Residue at	Glass transition
code	temperature	Change	649 ⁰ C	temperature (T _g)
	$T_d(^0C)$	(%)		(^{0}C)
				By DSC
PC	427.7	71.1	25.4	149.3
Н	434.3	69.4	26.0	141.3
Ι	442.4	68.1	26.5	138.9
J	446.6	67.8	27.5	144.5
K	450.5	67.0	27.9	148.3

6.2: Thermal Properties of PC/LCP/Kevlar blends:



Figure 6.2: TG plot of Pure PC (PC), PC/LCP (H), PC/LCP/ unmodified Kevlar (I), PC/LCP/ fluorinated Kevlar and PC/LCP/oxy-fluorinated Kevlar

This extent of enhancement of thermal stability on addition of LCP into PC matrix is attributed to the incorporation of the better thermally stable flexible chain polymers (LCP). Addition of Kevlar fiber further improves the thermal stability of the hybrid composites as the introduction of aromatic content of high thermal stability. Surface modification of Kevlar fiber further leads to the enhancement of the thermal stability of the PC/LCP blends (J. K) due to the incorporation of the functional groups on to the Kevlar surface resulting good compatibility between two polymeric species in case of fluorination and oxy-fluorination. Moreover, it is known that crystalline polymer is thermally more stable than its amorphous counter part due to energy input required overcoming both intermolecular and intermolecular forces. It is important to point out that the extent of more interaction in case of oxy-fluorinated Kevlar/PC/LCP blends due to more functional groups of oxyfluorinated Kevlar fiber can be responsible for a higher thermal stability of the oxy-fluorinated Kevlar fiber reinforced (composite R) composite as oxyfluorination generates controlled amount of long-living RO_2^* radicals.

6.4. X-ray study:

Figure 6.3 shows the X-ray parameters of the blend system. PC shows a broad spectrum near about $2\theta = 16.5^{\circ}$ due to the amorphous nature of the matrix polymer. Addition of LCP generates a very minute change in the X-ray pattern near about $2\theta = 19.5^{\circ}$, may be due to the LCP ($2\theta \sim 20^{\circ}$ C). From this we can infer that LCP is partially miscible with the amorphous PC matrix. The intensity of that small peak increases with the introduction of Kevlar fiber into the PC/LCP matrix. Which can be ascribed as the nucleating effect of Kevlar into the PC/LCP matrix and LCP/Kevlar induces very little crystallinity into PC.



Figure 6.3: X-ray diffraction pattern of Pure PC (PC), PC/LCP blend (H), PC/LCP/ unmodified Kevlar (I), PC/LCP/ fluorinated Kevlar (J) and PC/LCP/oxy-fluorinated Kevlar (K)

Surface modification of Kevlar further increases the intensity and shifts the peak to somewhat higher 2 θ value for this small peak ($2\theta = 19.75^{0}$) revealing better fiber matrix adhesion at the interface. This effect is more pronounced in case of oxy-fluorinated derivative.

6.5: Dynamic Mechanical Analysis (DMA):

Dynamic mechanical analysis is a significant tool for studying the relaxation in polymeric materials. Analysis of the storage modulus and tan δ curves is very utile in determining the performance of a material under stress and temperature. DMA not only appraises the dynamic mechanical attributes

of a material, but also detects changes in the solid structure of a polymer after compounding with other materials. Figure 6.4 and 6.5 display the dynamic mechanical profile (storage modulus E' and tan δ) as a function of temperature for PC/LCP/ Kevlar composites.

The storage modulus is closely related to the capacity of a material to absorb or return energy attributed to its elastic behavior (200). From Figure 6.4 it is very much evident that addition of LCP leads to the appreciable enhancement of the magnitude of storage modulus.



Figure 6.4:Storage modulus vs. temperature curve of i) Pure PC (PC), ii) PC/LCP blend (H), iii) PC/LCP/ unmodified Kevlar (I), iv) PC/LCP/ fluorinated Kevlar (J) and v) PC/LCP/oxy-fluorinated Kevlar (K)
This is ascribed to be due to the high intrinsic modulus of LCP phase consisting rigid rod like structure. Das et al (201) has reported the same observation in the PTFE/LCP blends. Figure 6.4 shows a sharp drop in storage modulus of every composite along with neat polymer corresponding to the glass transition temperature (T_g) . This modulus drop can be imputed to an energy dissipation phenomenon involving cooperative motions of the polymer chain. From Figure 6.4 also shows that with addition of Kevlar fiber into the PC/LCP blend further increases the storage modulus of the concerned blend, which may be due to the reinforcing nature of the Kevlar fiber into the PC/LCP matrix. Surface modification leads to the further enhancement of the magnitude of storage modulus of the fluorinated and oxy-fluorinated Kevlar fiber reinforced PC/LCP blend due to the incorporation of the reactive functional groups onto the Kevlar surface leading to better fiber matrix adhesion resulting the improved stiffness of the modified composites. This phenomenon is also supported by the results obtained from the XRD study where surface modification induces some crystallinity into the PC/LCP blend. Incase of oxy-fluorinated derivative this enhancement of storage modulus is more prominent.

The damping properties of the materials give the balance between the elastic phase and the viscous phase in a polymeric structure. The loss tangent (tan δ) of base polymer and their composites as a function of temperature is represented in Figure 6.5.



Figure 6.5: Tan delta vs. temperature curve of i) Pure PC (PC), ii) PC/LCP blend (H), iii) PC/LCP/ unmodified Kevlar (I), iv) PC/LCP/ fluorinated Kevlar (J) and v) PC/LCP/oxy-fluorinated Kevlar (K)

and the corresponding parameters are tabulated in Table 6.2. The glass transition temperature (T_g) is selected as the peak position of the tan delta curve when plotted against temperature. From Figure 6.5 it is evident that all the composites along with the pure polymer show a single peak near about 160^oC, which is the glass transition temperature of the PC matrix polymer. In case of PC/LCP/ Kevlar composites the loss peak broadens may be due to the overlapping peak of PC and LCP, which suggests the partial miscibility of the LCP with PC matrix phase as mentioned earlier. The broadening of loss peak

in the presence of fiber can also be ascribed to matrix-fiber (filler) interaction. The matrix polymer (PC/LCP) in the adjacent portion of the fiber can be considered to be in different state in comparison to the bulk matrix, which can disturb the relaxation of the matrix resulting in a broad tan δ peak T_g value shifted to the lower temperature side in case of PC/LCP (H) in comparison to the pure matrix (PC) may be due to the partial miscibility of PC with LCP. In case of PC/LCP/ unmodified Kevlar (I), the magnitude of Tg further decreases may be due to the poor fiber/matrix adhesion at the interface. Fluorination and oxy-fluorination of Kevlar fiber enhances the glass transition temperature appreciably in case of the concerned composites (J, K). This can be ascribed as the better fiber/matrix adhesion at the interface due to the incorporation of reactive groups on the fiber surface. The relative decrease in the height of tan δ peak related the increase in the extent of crystalline properties imposed by the LCP and Kevlar fiber in the polymers since the transition behavior is associated with the local mobility of polymer chains in the amorphous region of the polymer, which is also reflected in the increase of storage modulus of the samples. More over, the Tg values obtained from the two techniques (DSC and DMTA) are different because of the sensitivity difference between the two methods towards the glass transition temperature and also mentioned in literature (181).

6.6. SEM study:

From the micrograph [Figure 6.6 (a-d)] of PC/LCP and PC/LCP/Kevlar blends, it is apparent that with addition of LCP the fibrillation of LCP occurs

in the PC matrix (Figure 6.6a). Incorporation of Kevlar induces the fibrillation of the LCP in the PC phase resulting enhanced properties of the PC/LCP/Kevlar composites although the Kevlar fibers are covered by the matrix (Figure 6.6b).





b



с

d

Figure 6.6: a) SEM picture of PC/LCP blend (H), ii) SEM picture of PC/LCP/ unmodified Kevlar (I), iii) SEM picture of PC/LCP/ fluorinated Kevlar (J) and iv) SEM picture of PC/LCP/oxy-fluorinated Kevlar (K).

In case fluorinated Kevlar reinforced composites (J, Figure 6.6c) the LCP fibrils are more prominent and distributed through out the matrix phase but appeared as bundle form. On the other hand oxy-fluorinated derivative (K, Figure 6.6d) exhibits fine micro fibrils are homogeneously dispersed all over the PC matrix phase giving rises to best properties amongst all composites.

6.7. Simulation of fiber orientation by mold flow simulation technique:

Simulation of fiber orientation of PC/LCP/Kevlar composites under different injection molding condition was performed using mold flow simulation technique and the corresponding processing parameters are given below in Table 6.6:

Sample Code	$T_{m}(^{0}C)$	T _{mold} (⁰ C)	Flow rate (cm ³ /s)
Series I1/	200	(0	20
Series J1/ Series K1	300	60	20
Series I2/ Series J2/ Series K2	320	40	48
Series I3/			
Series J3/ Series K3	320	40	20
Series I4/	220	(0)	•
Series J4/ Series K4	320	60	20

Table 6.6: Processing parameters for injection molding:

In order to understand the fiber orientation in PC/LCP/ unmodified, fluorinated and oxy-fluorinated Kevlar under different processing parameters mold flow simulation technique has been used. The variation of orientation tensor with different normalized thickness under different processing parameters have been displayed in Figure 6.7 (a-c) and corresponding orientation pattern under different normalized thickness have been depicted in Figure 6.8 (a-d), 6.9 (a-d) and 6.10 (a-d).

From Figure 6.7(a-c) and 6.8a i, ii, iii, d i, ii, iii; 6.9a i, ii, iii, d i, ii, iii and 6.10a i, ii, iii, d i, ii, iii, it is very much evident that melt temperature (I1, Figure 6.7a, 6.8a i, ii, iii; J1, Figure 6.7b, 6.9a i, ii, iii; K1, Figure 6.7c, 6.10a i, ii, iii and I4, Figure 6.7a, 6.8d i, ii, iii; J4, Figure 6.7a, 6.9d i, ii, iii and K4, Figure 6.7a, 6.10d i, ii, iii) has pronounced effect on the fiber orientation of PC/LCP/ Kevlar composites in both the skin and core region. Although the fiber orientation exhibits similar trend in the core as well as in skin region at both higher and lower melt temperature.



Figure 6.7a) Fiber orientation tensor vs. normalized thickness of PC/ LCP/ unmodified Kevlar (I) under different processing parameters (1, 2, 3, and 4)

The fibers are more oriented in the core region (higher magnitude of orientation tensor) than that of the skin. However, higher melt temperature possess some what less fiber orientation tensor than that of the lower variable.



Figure 6.7b) Fiber orientation tensor vs. normalized thickness of PC/ LCP/ fluorinated Kevlar (J) under different processing parameters (1, 2, 3, and 4)



Figure 6.7c) Fiber orientation tensor vs. normalized thickness of PC/ LCP/ oxy-fluorinated Kevlar (K) under different processing parameters (1, 2, 3 and 4)

Figure 6.7(a-c) and 6.8a i, ii, iii, b i, ii, iii; 6.9 a i, ii, iii, b i, ii, iii and 6.10a i, ii, iii, b i, ii, iii exhibit the fiber orientation in the PC/LCP/ Kevlar composites under varying flow rate. From those Figures it is evident that flow rate has significant effect on the fiber orientation of the composites. At lower flow rate more fibers are orientated in the skin region in flow direction (evidenced from orientation tensor value) (I3, Figure 6.7a, 6.8c i, ii, iii; J3, Figure 6.7b, 6.9c i, ii, iii; and K3, Figure 6.7c, 6.10c i, ii, iii) than that of higher counter part (I2, Figure 6.7a, 6.8b i, ii, iii; J2, 6.7b, 6.9b i, ii, iii; and K2, 6.7c, 6.10b i, ii, iii).



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Figure 6.8a) Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.834123), ii) core region (normalized thickness= 0, T_{xx} = 0.891039), iii) top surface (normalized thickness = 1, T_{xx} = 0.834123) of unmodified Kevlar / PC/ LCP composites (SeriesI1).



Figure 6.8b) Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.689984), ii) core region (normalized thickness= 0, T_{xx} = 0.759418), iii) top surface (normalized thickness = 1, T_{xx} = 0.689984) of unmodified Kevlar /PC/LCP composites (SeriesI2).

This can be ascribed as an increase in the mold wall –polymer contact time at lower flow rate leading to a thick solidified layer i.e. the skin structure.

This solidified skin layer high shear flow field at the solid-melt interface. Such a shear flow orients the fibers in flow direction.





Orientation in the flow direction increases with increasing shear rate. On the other hand, the long contact time provided by the low injection speed results in the thicker skin structure and in preservation of the fiber orientation patterns in the concerned zone (i.e. skin region).



Figure 6.8d) Fiber orientation at the i) bottom surface (normalized thickness = -1, T_{xx} = 0.724652), ii) core region (normalized thickness= 0, T_{xx} = 0.76954), iii) top surface (normalized thickness = 1, T_{xx} = 0.724652) of unmodified Kevlar /PC/LCP composites (SeriesI4)

An interesting trend of fiber orientation has been observed in case of varying mold temperature (I3, J3, K3 and I4, J4, K4) Figure 6.7 (a-c) and Figure 6.8 c, d; 6.9 c, d; and 6.10 c, d. At higher mold temperature more fibers are oriented in core region than that of the skin (greater orientation tensor value) and in case of lower mold temperature the opposite trend has been observed.



Figure 6.9a) Fiber orientation at the i) bottom surface (normalized thickness = -1, T_{xx} = 0.904304), ii) core region (normalized thickness= 0, T_{xx} = 0.927326), iii) top surface (normalized thickness = 1, T_{xx} = 0.904304) of fluorinated Kevlar /PC/ LCP composites (Series J1).



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Figure 6.9b) Fiber orientation at the i) bottom surface (normalized thickness = -1, $T_{xx} = 0.820934$), ii) core region (normalized thickness= 0, $T_{xx} = 0.830934$), iii) top surface (normalized thickness = 1, $T_{xx} = 0.820934$) of fluorinated Kevlar /PC/ LCP composites (Series J2).

For high mold temperature, the temperature difference between the molten fluid and mold temperature leads to the thinner solidified skin leading to the lower flow field at the solid-melt interface and lower shear rates in the solid-melt interface thus orienting lesser fiber in the flow direction in the skin region.



Figure 6.9c) Fiber orientation at the i) bottom surface (normalized thickness = -1, T_{xx} = 0.884709), ii) core region (normalized thickness= 0, T_{xx} = 0.840919), iii) top surface (normalized thickness = 1, T_{xx} = 0.884709) of fluorinated Kevlar /PC/ LCP composites (Series J3).



Figure 6.9d) Fiber orientation at the i) bottom surface (normalized thickness = -1, $T_{xx} = 0.884479$), ii) core region (normalized thickness= 0, $T_{xx} = 0.890948$), iii) top surface (normalized thickness = 1, $T_{xx} = 0.884479$) of fluorinated Kevlar /PC/ LCP composites (Series J4).







Figure 6.10b) Fiber orientation at the i) bottom surface (normalized thickness = -1, T_{xx} = 0.630386), ii) core region (normalized thickness= 0, T_{xx} = 0.702878), iii) top surface (normalized thickness = 1, T_{xx} = 0.630386 of oxy-fluorinated Kevlar /PC/ LCP composites (Series K2)



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Figure 6.10c) Fiber orientation at the i) bottom surface (normalized thickness = -1, T_{xx} = 0.740444), ii) core region (normalized thickness= 0, T_{xx} = 0.641091), iii) top surface (normalized thickness = 1, T_{xx} = 0.740444) of oxy-fluorinated Kevlar /PC/ LCP composites (Series K3).



Figure 6.10d) Fiber orientation at the i) bottom surface (normalized thickness= -1, T_{xx} = 0.639416), ii) core region (normalized thickness= 0, T_{xx} = 0.699416), iii) top surface (normalized thickness = 1, T_{xx} = 0.639416) of oxy-fluorinated Kevlar /PC/ LCP composites (Series K4)

However, MOLDFLOW does not consider fiber/matrix adhesion in their program. As mentioned earlier that it uses the Folgar-Tucker model, which is a modification of the Jeffery model by adding a diffusive term to consider the fiber-fiber interaction. In the Jeffery model, inertia and Brownian motion of the fibers are neglected. The fibers the Jeffery model considers are rigid particles moving in a Newtonian fluid, which - however - do not disturb the motion of the fluid. So it is not important whether the fiber/matrix adhesion is good or not in mold flow technique.

Chapter: 7

Summary and Conclusions

Summary and Conclusions

A symmetric study on the development of fluorinated and oxyfluorinated short Kevlar fiber reinforced thermoplastic composites and comprehensive characterizations have been carried out.

Effect of fluorinated and oxy-fluorinated short Kevlar fiber on the properties of ethylene propylene matrix composites

The thermomechanical properties of composites containing EP and surface treated and untreated Kevlar fiber have been explored. The thermal studies showed that thermal stability as well as storage modulus of the composites has been increased due to the reinforcement of fiber and it gradually continued in case of fluorinated and oxy-fluorinated Kevlar fiberreinforced EP, which attained maximum value in case of oxy-fluorinated derivative. Although the tensile strength of original Kevlar fiber reinforced EP (B) decreased in comparison to pure EP, tensile strength of fluorinated and oxy-fluorinated Kevlar fiber/EP (E and H, respectively) composite increased appreciably. Thus, fluorination and oxy-fluorination of the fiber influenced the surface morphology of the fiber, resulting in better adhesion between the fiber and the matrix.

Compatibilizing effect of MA-g-PP on the properties of fluorinated and oxy-fluorinated Kevlar fiber reinforced ethylene polypropylene composites

The effect of compatibilizer on the properties of the untreated, fluorinated and oxy-fluorinated Kevlar /EP composites have been explored. Improved thermal, dynamic mechanical, crystalline as well as rheological properties of the compatibilized systems have been observed. These enhanced properties can be ascribed as the better adhesion between the fiber and matrix due to the incorporation of the MA-g-PP into the EP matrix. Oxy-fluorinated Kevlar /EP composites exhibit superior properties amongst all the composites because of the generation of the peroxy radical on to the Kevlar surface and also reactive groups on the EP matrix (due to MA-g-PP) resulting the strong interaction at interface which is absent in case of fluorinated counterpart. At higher MA-g-PP content the enhancement of the properties of composites are not very much pronounced.

Effect of fluorinated and oxy-fluorinated Kevlar fiber loading on the properties of EP/Kevlar composites

EP-containing modified Kevlar fibers show better crystalline, dynamic mechanical and thermal properties than other composites with the same unmodified Kevlar fiber loading. This effect is much more pronounced in case of oxy-fluorinated Kevlar/EP composites. The polar functional groups on the Kevlar fibers surface played an important role in accelerating both the dispersion of Kevlar fibers and the interfacial adhesion in the composites compared to unmodified fibers.

Properties of Syndiotactic Polystyrene Composites with Surface Modified Short Kevlar Fiber The effects of addition of fluorinated and oxy-fluorinated short Kevlar fiber on crystalline, thermal, dynamic mechanical and morphological properties of syndotactic PS have been investigated. The incorporation of the short Kevlar fiber effectively enhances the crystallization of the PS matrix through heterogeneous nucleation, and the nucleation effect is more evident in case of fluorinated short Kevlar fibers. A homogeneous dispersion and a strong interfacial adhesion between oxy-fluorinated Kevlar fiber and the s-PS matrix are better than other composites evidenced by scanning electron microscopy and atomic force microscopy, which brings an enhancement in the storage modulus and thermal stability of the composite. So, the more functional groups on the Kevlar fiber surface play an important role in preparation of composites with s-PS matrix.

Study on the Mechanical Rheological and Morphological Properties of Short Kevlar Fiber/s-PS Composites- effect of oxy-fluorination of Kevlar

Mechanical, rheological and dynamic mechanical properties of the unmodified and modified short Kevlar fiber reinforcement in the s-PS matrix have been studied. Kevlar fiber reinforcement improves the dynamic mechanical and rheological property of the untreated composite but reduces mechanical properties. Oxy-fluorinated Kevlar fiber reinforcement significantly affect the surface morphology of that particular composite resulting better dynamic, mechanical and rheological properties. These enhanced properties of the oxy-fluorinated Kevlar fiber reinforced s-PS is attributed to the improved interfacial adhesion between the fiber and the matrix generating from the incorporation of the functional group on to the Kevlar surface.

Simulation of the Fiber Orientation of Kevlar in s-PS/ Kevlar Composites- Effect of fluorinated and oxy-fluorinated Kevlar Fiber on the Properties and Processibility

Various physico-chemical properties of unmodified and modified (fluorinated) Kevlar/ s-PS composites under different processing parameters have been studied. Modified polymer composites exhibit better thermal as well as crystalline properties in comparison to the unmodified composite as evidenced from differential calorimetric study and X-ray diffraction study due to better adhesion between fiber and the matrix at the interface. Thermal and crystalline properties of the composites remarkably vary with the processing parameters. There is an optimum condition under which composites along with the virgin polymer possess superior crystalline and thermal properties. Simulation of the fiber orientation has been performed using mold flow technique and the variation of magnitude of the orientation tensor with the normalized thickness has been reported, which clearly depicted that fiber orientation varies very significantly with the processing parameters in the skin as well as in the core region. SEM micrographs show more surface adhesion in case of modified Kevlar/s-PS composites.

Effect of fluorinated and oxy-fluorinated short Kevlar fiber reinforcement on the properties of PC/LCP blends

Effect of fluorinated and oxy-fluorinated Kevlar fiber reinforcement into PC/LCP blend has been explored. LCP enhances the thermal stability of the PC/LCP blends and further improvement of thermal stability has been observed by introducing Kevlar fiber into the PC/LCP system due to the incorporation of high thermally stable aromatic content. Surface fluorination and oxy-fluorination again enhances the thermal stability of the modified systems due to the incorporation of functional groups on to the Kevlar surface resulting better fiber/matrix adhesion. Incorporation of LCP into the amorphous PC matrix induces some crystallinity of the matrix phase and the crystalline property is further enhanced by the incorporation of unmodified and modified Kevlar fiber reinforcements due to the nucleating ability of the concerned fiber. DSC heating scan exhibits the double humped curve (glass transition temperature) in case of PC/LCP system indicating the partial miscibility of constituent materials. Incorporation of Kevlar fiber into the PC/LCP system shifted the glass transition temperature towards the lower temperature side due to the poor fiber/matrix adhesion at the interface. Surface modification (by fluorination and oxy-fluorination) enhances the glass transition temperature due to the batter fiber/matrix bonding at the interface as a result of introduction of functional groups onto the Kevlar surface as evidenced from DSC and DMA study. Storage modulus of the PC/LCP system increases in comparison to the pure matrix. Kevlar fiber reinforced systems possess better dynamic mechanical behavior as evidenced from DMA study. Fluorinated and oxy-fluorinated Kevlar fiber reinforcement results in the further enhancement of the storage modulus of the resulting composites because of the better fiber/matrix adhesion at the interface. Scanning Electron Microscopy reveals the fine fibrillation of the LCP phase in the PC matrix in presence of oxy-fluorinated Kevlar fiber reinforced derivative leading to the best thermal, dynamic mechanical and crystalline properties. Mold flow simulation technique reveals that fiber orientation is different in the skin and the core region under different processing parameters.

Conclusions:

From the entire study it is revealed that fluorinated and oxy-fluorinated short Kevlar fiber reinforcement into the various thermoplastic matrices leads to the better thermal, mechanical and dynamic properties of the concerned composites in comparison to the unmodified counterpart. This is because of the surface modification of the Kevlar fiber by fluorination and oxy-fluorination which leads to the generation of the functional groups on the Kevlar surface resulting better adhesion between the fiber and the matrix. The improvement of the properties is much more pronounced in case of oxy-fluorinated composites. In fluorination, polymeric materials are treated with fluorine or fluorine-inert gas mixture. In this case hydrogen atoms are substituted by fluorine, double and conjugated bonds are saturated with fluorine. The presence of oxygen during the fluorination (oxy-fluorination) of hydrocarbons leads to the formation of various oxygen functionalities such as carbonyl groups, carboxyl acids, peroxides, hydroxyl groups, and acid fluoride groups. These more functional groups and long living free radicals (RO₂) which in turn may be responsible for graft polymerization giving rise to the best adhesion between the fiber surface and the matrix as a result the thermal, mechanical and dynamic properties of the oxy-fluorinated Kevlar fiber reinforce thermoplastic composites improves appreciably.

Various physico-chemical properties have studied under different injection molding parameters of s-PS/ Kevlar composites. Results showed that the properties are very much dependent on the processing parameters. There is

an optimum processing condition under which all the composites show superior properties. High rate of injection speed is accompanied with high crystallinity, low interplaner spacing and high crystallite size for all the composites. Higher mold temperature possesses higher crystallinity, lower interplaner spacing, and higher crystallite size. Higher melt temperature leads to slightly lower crystalline properties of the composites.

Thermal, dynamic mechanical and crystalline properties of the PC/ LCP/ Kevlar composites have been studied. Effect of fluorination and oxyfluorination on those aforementioned properties has also been discussed over here.

Mold flow simulation technique was applied to evaluate the fiber orientation in injection molded s-PS/ Kevlar, PC/ LCP/ Kevlar composites. This technique reveals that the fiber orientation is different in core and the skin region. Moreover, processing parameters significantly affect the fiber orientation pattern in the skin and that of the core region. References



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Glossary

EP	Ethylene Propylene Polymer
MA-g-PP	Maleic anhydride grafted polypropylene
MA-g-PE	Maleic anhydride grafted polyethylene
РРТА	p-Poly (phenyl terephthalamide)
SPS	Syndiotactic polystyrene
PC	Poly carbonate
LCP	Liquid crystalline polymer
T_g	Glass Transition Temperature
T _m	Melting Temperature
T _c	Crystalline Temperature
\mathbf{E}'	Storage modulus
$\mathbf{E}^{\prime\prime}$	Loss modulus
T _{XX}	Orientation tensor
Phr	Parts Per Hundred Rubber
ASTM	American Standard for Testing Materials
FTIR	Fourier Transform Infrared
XRD	X-ray Diffraction
DTA	Differential Thermal Analysis
TGA	Thermo-gravimetric Analysis
SEM	Scanning Electron Microscopy
DSC	Differential Scanning Calorimetry
DMTA	Dynamic Mechanical Thermal Analysis
AFM	Atomic Force Microscope



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