INVESTIGATION ON MECHANICAL AND WEAR PROPERTIES OF COMPOSITE FROM RECYCLED POLYMER FOR GEARS WITH OPTIMIZED COMPRESSION MOULDING

Thesis

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

By

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May, 2014

Dedicated to

my parents,
teachers and
my mother land

NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA, SURATHKAL

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C E R T I F I C A T E

This is to *certify* that the Research Thesis "**INVESTIGATION ON MECHANICAL AND WEAR PROPERTIES OF COMPOSITES FROM RECYCLED POLYMER FOR GEARS WITH OPTIMIZED COMPRESSION MOULDING**" submitted by **B. Krishna Prabhu** (Register Number: **090684ME09P02)** as the record of the research work carried out by him, is *accepted as the Research Thesis submission* in partial fulfillment of the requirements for the award of degree of **Doctor of Philosophy.**

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ACKNOWLEDGEMENT

ABSTRACT

Cost of a product can be visualized as sum of the cost of materials and process cost. In a competitive world, producing quality products at low cost is need of the day. In reducing the process cost, the use of off line techniques like Design for manufacturing (DFM), design of experiments (DOE), Six Sigma optimization and process modeling could be adopted. Further, judicious development of low cost materials, will help in bringing down the total cost of the product. In view that polymer consumption is growing at a fast pace, reusing post consumer polymers could help reducing the material cost component of the product. Recycling engineering plastic such as post consumed Polyethylene Terephthalate (PET) provides not only a cheap and abundantly available source of material but also expands the sphere of application for recycled PET (r-PET). However, owing to reduction in the properties due to recycling procedures, the plastic need to be developed suitably, to meet the requirements of an application. Reinforcing r-PET with suitable material could address this issue. Fly ash cenospheres are low cost material that could be useful in improving the properties of recycled polymers. The cost of the product developed from low cost recycled materials could be further reduced by developing suitable low cost process. Compression moulding could be a low cost process. The process however needs to be optimized for moulding product with appreciable quality.

Thus the present study is focused on developing r-PET based composites with FA cenospheres as reinforcement and compression moulding as a manufacturing process in order to cater the requirements of an industry to produce low cost engineering components such as gears. In the process of optimization, Six Sigma based DMAIC/DMADV methodology along with Taguchi's method and RSM are utilized where as development of r-PET/FAC composite is carried out using design of experiments (DOE). Entire work is envisaged in five stages

The first stage of the experimentation is carried out with an intention to establish a thermo-mechanical moulding process for r-PET. Six Sigma DMADV methodology is utilized along with Failure Modes and Effects Analysis (FMEA) for successive improvement in the moulding procedure. A reduction in risk priority number (RPN) from 900 to 315 and finally to 8 is achieved on successive improvement in the process using FMEA. At the end of its successful application, a good, repeatable sample quality is achieved.

In the second stage, R-PET, reinforced with FAC is studied for a set of compression moulding process variables and material variables using DOE as statistical tool. Five factors, critical to quality (CTQs) viz. moulding pressure (5, 10, 15 MPa); moulding time (5, 10, 15 min.); mould cooling (water, air, water and air); moulding temperature (50, 100, 150 °C) and weight fraction of cenospheres (5, 10, 15%), are considered at three levels. The DOE methodology adapted for such investigations showed a down ward trend for FAC content. The cause investigated using fractographic analysis, concludes debonding of FAC from the matrix due to improper interfacial characteristics. Further, the composite underwent brittle fracture making it not much useful for gear applications. The remedy considered for developing r-PET composite that makes it suitable for the gear application is to blend the matrix with an appropriate recycled polymer and to improve interfacial interactions of FAC with matrix by suitably treating FAC with (3-Aminopropyl) trimethoxy silane (3APTMS). The wear property of the composite however, proves promising as FAC reduced Specific wear rate (SWR).

The preliminary work in developing the matrix, in the third stage, involves blending r-PET with five softer polymers from recycled regime. R-LLDPE, r-LDPE, r-HDPE, r-PP and r-Nylon are these five polymers. Experimentation of r-PET blends suitably selects r-LDPE as better suited polymer owing to its flexural and wear properties. . Blending r-PET with 10% r-LDPE improves the toughness by 100% and by 112% at 30%. This is followed by r-HDPE that shows 25% and 100% increase at respective composition. Flexural strength and SWR of r-PET/r-LDPE blends affected marginally when

compared to the plastics considered in this study. The next part of third stage involves developing the composite with matrix blended with r-LDPE (30% by wt.), reinforced with FAC (5, 10, 15% by wt). An improvement in the fracture strain, over 87 % is noted at 30% of r-LDPE and 15% FAC. An improvement in toughness by about 66 MPa at 5% FAC and 13 MPa at 30% of FAC is observed. Thus studies on matrix blending conclude that blending r-PET with r-LDPE helps in reducing the brittleness of r-PET. Further, 3APTMS (6, 8, 10% by wt.) is used for treating FAC and to improve the interface. Reinforcing r-PET with 3APTMS (10% by wt.) treated FAC (T-FAC) improved flexural strength of r-PET/T-FAC composite. An increase of 34% strength at 5% T-FAC, 57% increase at 10% and 120% improvement in strength at 15 % of T-FAC is observed owing to surface treatments given to FAC. Such an increase in the properties leads to improvement in the toughness of the composite. Toughness improves by 95% at 5% of T-FAC, 200% at 10% and an increase of 271% in toughness when r-PET is reinforced with 15% T-FAC is observed. Owing to blending and treating of reinforcement, flexural and wears properties improved significantly. Further M-r-PET/T-FAC composite is also tested for their properties. The results of M-r-PET/T-FAC composite conclude favorably for developing low cost material from recycled means. In the next stage, the process and material thus developed are optimised for flexural and wear properties.

In the fourth stage the process and material parameters are optimized for improved properties of the composite. Six Sigma DMAIC optimisation tool, Analysis of variance (ANOVA), Response surface methodology (RSM) are used to determine the optimum values. The final optimum parameters for moulding r-PET reinforced with FAC are Moulding pressure – 11.2 MPa, 3APTMS -7.9 % by wt., r-LDPE - 29 % by wt., moulding Temperature - 52.6 ºC and FAC – 12.5%. Confirmation experiments for these optimum values are done to verify the validity of the process adopted.

In the fifth and final stage the material developed in the previous stages is moulded into gears with optimized compression moulding and their performance is evaluated on an indigenously designed and fabricated gear test rig. The increase in the gear life by about

275% w. r .t the starting composite (r-PET/FAC) seems good for the applications sought for them. The gear can handle a load of about 30.5 N and can take about 50,000 revolutions. With such an improvement shown by the composite material developed in this work, it could be considered as an alternative to the existing gears made from neat polymers for lower loading applications. Thus the objectives set for this research work that to develop a low cost composite material from environment hazardous waste materials with optimized compression moulding for gear applications are met with the systematic application of Six Sigma methodologies as explained in this work.

Key words: Recycled PET, r-LDPE, Cenospheres, r-PET composites, Mechanical and wear properties, Six Sigma DMAIC/DMADV, Design of experiments, Polymer Gears.

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Abbreviations

ANOVA: Analysis of variance

CMC: Ceramic matrix composites

CTQ: Critical to quality

DMAIC: Define, Measure, Analyze, Improve and Control methodology

DMADV: Define, Measure, Analyze, Design and Verify methodology

DOE: Design of experiments

DFM: Design for manufacturing

DOF: Degrees of freedom

FA: Fly ash

FAC: Fly ash cenospheres

FMEA: Failure modes and Effects Analysis

FTIR: Fourier transformation infra red spectroscopy

IEN: Interpenetrating elastomeric networks

LVDT: Linear Variable Differential Transformer

K_0: Specific Wear Rate (SWR)

MMC: Metal matrix composite

M-r-PET: Matrix modified recycled Poly (ethylene terephthalate)

M-r-PET/FAC: Modified r-PET matrix, reinforced with FAC

M-r-PET/T-FAC: Blended r-PET matrix, reinforced with treated FAC

MS: Mean square

MT: Metric Ton

MMT: Million Metric Ton

MPa: Mega Pascal

N: Newton

OA: Orthogonal array

PE: Poly ethylene

PVC: Poly vinyl chloride

PP: Poly propylene

PS: Poly sulphone

PET: Poly (ethylene terephthalate)

PMC: Polymer matrix composite

r-PET: Recycled Poly (ethylene terephthalate)

r-PET/FAC: r-PET matrix reinforced with FAC

r-PET/T-FAC: r-PET matrix reinforced with treated FAC

r-LDPE: recycled low density polyethylene

r-LLDPE: recycled linear low density polyethylene

r-HDPE: recycled high density polyethylene

r-PP: recycled polypropylene

r-Nylon: recycled Nylon

RPN: Risk Priority Number

RSM: Response surface methodology

Rpm: Revolutions per minute

SIN: Simultaneous interpenetrating polymer networks

SS: Sum of squares

S/N: ratio of mean to variance

SWR: Specific wear rate

T-FAC: Treated fly ash cenospheres (Treated with 3APTMS)

TGA: Thermo gravimetric analysis

Tg: Glass transition temperature

UTM: Universal testing machine

3APTMS: (3-Aminopropyl) trimethoxy silane

CHAPTER 1

INTRODUCTION

In an ever growing competitive market, manufacturing quality products at possible minimum cost is essential. The two major contributors for the cost of a product are process cost and material cost. Process cost could be reduced by techniques like Design for manufacturing (DFM), Design of experiments (DOE), Six Sigma optimization, Process Modeling etc. (Sanjay 2002). Systematic selection or development of low cost material will further reduce the total cost of the product. Presently product developers have the luxury of adopting both approaches to reduce product cost.

In the past, steel and aluminum were commonly used for engineering products. With increasing customer demand for energy efficient, low cost and functional products, new material systems such as composites are developed. (Vaill 1962). The concept of composite materials is ancient and even natural. Mud reinforced by straw in the bricks, composite bows used by Pigmies etc. are a few ancient examples for composites. Wood, animal bones are the best examples of natural composites. Composites with metal matrix are potentially applied in the aeronautical industries for realizing higher thrust levels, lighter weight, and increased efficiency (Hooker and Doorbar 2004). Composites with ceramic matrix (CMC) have been in use for the past 20 years for high temperature applications in industrial gas turbines (Mark 2004). On the other hand polymers, blends and their composites are developing at least 15 − 20% more intensively than that of the ceramic and metal industry. Such huge production of polymers put forward the tasks for improving quality of the articles made from them for extending the field of their applications (Mikitaev 2006).

1.1 COMPOSITES AND THEIR CLASSIFICATION

A composite is a macroscopic combination of two or more distinct materials, having a recognizable interface between them (Ever 1996, ASTM D3878). The components of the composite are combined in such a way so as to enhance their virtues while lowering their shortcomings. By combining distinct materials, one can optimize the properties of the

composite. By definition "Composite is a synthetic assembly of at least two macro constituents which are insoluble into each other and are chemically distinct on macroscopic scale, but nevertheless act in concept to yield superior properties". Composite is one, which satisfies the following conditions as per Chawla (2001):

- It is manufactured or man-made (synthetic).
- It consists of two or more physically and/or chemically distinct, suitably arranged or distributed phases with an interface separating them.
- It has characteristics that are not depicted by any of the constituents examined in isolation.

Composite in its two constituent forms consist of a discontinuous phase embedded in a continuous medium. The discontinuous phase usually is a reinforcing material embedded in a continuous matrix (binder). The matrix being a continuous medium plays a primary role of keeping the aggregates of discontinuous phase (reinforcements) in the bound form and transfer load to the reinforcements (Hull and Clyne 1996). The matrix also acts as a barrier to protect reinforcements against adverse environment and mechanical/chemical degradation like abrasion or corrosion. Reinforcement is a discontinuous or distributed phase that possesses superior properties and bears the load, especially during the instances of mechanical loading. Load transfer takes place from matrix to reinforcement due to an interaction between reinforcement and matrix (Broutman and Krock 1974).

In the context of toughness and strength of the composite, the role of the matrix is more subtle and complex than that of the reinforcements involved. Many reinforcing components like glass, graphite and boron fibers can produce a tougher material via a synergism achieved by a combination of mechanisms. Optimization of stiffness and strength of composites is still one of the unresolved main objectives and is under serious consideration. (Güneri Akovali, [ed] 2001).

Composites are classified according to either of the constituents, the matrix or the reinforcement. Based on the matrix material, composites can be classified as Metal matrix composite (MMC), Ceramic matrix composite (CMC) and Polymer matrix composite (PMC). PMC's are becoming promising materials for various structural and automotive applications since these possess favorable combinations of mechanical

properties (Suresha et al. 2007). Metal and ceramic matrix composites find few applications when compared to PMC's, because of the involved processing methods and high cost. The applications of the former two varieties are typically seen in high performance/high temperature and cost intensive categories (Patil 2006). On the other hand, PMC's have wider usage and attract a lot of interest due to their relative ease of processing, low density, desirable electrical/thermal properties and excellent chemical/corrosion resistance. Hence, these find wide applications ranging from specialized functions in aerospace and electronics engineering to day-to-day consumer industries like construction and transport. The polymer matrix composites especially meet the cost, weight and corrosion resistant qualities to a great extent. Thus there exists a huge focus for developing new polymer matrix composites.

1.2 POLYMER MATRIX COMPOSITES

Polymer matrix composites use polymer as their matrix with a wide range of reinforcements. Ever since the invention of the first polymer, the natural rubber in 1839 by Charles Goodyear, the world has seen wide varieties of both natural and synthetic polymers. The details of a few such inventions are mentioned in Table 1.1. Most of them have been used in PMC's.

In the packaging and distribution of food stuffs and other perishable commodities the commercial thermoplastic polymers used are hydrophobic and biologically inert thus making them essential for modern retailing (Scott 1999). Companies utilize these new materials to retain cost and quality. The requirements of industries like lightweight, better strength, ease of forming and non-corrosiveness have given rise to several developments in composites technology (Srinivasan and Ramakrishnan 1983). Further, transforming polymer composites to near-net-shape parts using simple and low-cost tooling is easier and much well known. Moulding is one such technique. There are two major benefits in producing near-net or net-shape parts using moulding techniques. First, it minimizes the machining requirement and thus the cost of machining. Second, it minimizes the scrap and thus provides material savings.

Table 1.1: Time line for the inventions of some polymers

Plastic	Year of Invention.	Inventor
Natural Rubber	1839	Charles Goodyear
Polystyrene	1839	Eduard Sion
Vulcanite	1843	Thomas Hancock
Gutta-Percha	1843	William Montgomerie
Shellac	1856	Alfred Critchlow, Samuel Peck
Bois Durci	1856	Francois
Parkesine	1862	First man made plastic
Celluloid	1863	John Wesley Hyatt
Polyvinylcloride	1872	Eugen Baumann
Viscose Rayon	1894	Charles Frederick Cross & Edward John Bevan
Phenol-formaldehyde	1899	Arthur Smith
Bakelite	1907	Leo Hendrik Baekeland
Cellophane	1908	Jacques E. Brandenberger
Addition and Condensation polymers	1929	Wallace Hume Carothers
Plastisizing & moulding of PVC	1929	Waldo Semon
Polymethylmethacrilate	1932	John Crawford
Polythene	1933	Eric Faweett & Reginald Gibson
Polyvinylidene cloride	1933	Ralph Wiley
Low-density polyethylene	1935	Reginald Gibson and Eric Fawcett
Polymethyl Methacrylate	1936	
Polyurethanes	1937	Otto Bayer and co-workers
Polytetrafluoroethylene	1938	Roy Plunkett
Nylon	1939	
Neoprene	1939	
Poly (ethylene terephthalate)	1941	John Rex Whinfield &
Terylene	1941	John Rex Whinfield & James Tennant Dickson
Viscoelastic Polymers	1943/1949	James Wright/ Peter Hodgson
High-density polyethylene	1951	Paul Hogan and Robert Banks
Polypropelene	1951	Paul Hogan and Robert Banks
Styrofoam	1954	Ray McIntire
Kevlar	1963	Stephanie Kwolek
Polyimide	1964	
Thermoplastic Polyester	1970	Mylar, Melinex, Teijin, and Tetoron
Linear Low Density Polyethylene	1977	

The use of polymer composites in the manufacturing arena has the following advantages:

- Large quantities of it can be moulded at less expense.
- Cams, bearings, ratchets and gear shafts can be designed as integral parts to reduce cost of assembly and defects during assembly.
- Multiple gears of several diameters and tooth size can be moulded as a single unit to reduce costs.
- Tolerances are less critical for smooth and quiet performance due to the inherent resilience of plastics gears that causes them to conform to differences in pitch and profile.

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- Their resilience causes them to damp moderate shocks or vibrations.
- Efficiency performance is obtained due to their low coefficient of friction.
- Inertia/torques on gears are less because of lower density.
- Little or no lubrication is required.
- They can operate in corrosive ambience.

However, they have following limitations
- Their maximum load-carrying capacity is significantly lower.
- Their load-carrying capacity decreases as temperature increases (with an upper temperature limit of about 120°C).
- Since these materials have higher thermal coefficients of expansion, plastics gears are more dimensionally sensitive.
- They cannot be produced to high precision.
- Not much is known about their complex thermo-mechanical behaviour.

As mentioned earlier, the two components of any composite are matrix and the reinforcement. Availability of both these components in wide varieties makes it possible to have a wide spectrum of composite to meet the precise need of an application. The following sections are focused on deliberating matrix and reinforcing materials for polymer composites.

1.3 MATRIX MATERIALS FOR POLYMER MATRIX COMPOSITES

Polymers are long chain organic molecules or macromolecules with many desirable properties such as high ductility, ease of forming and non-corrosiveness (Srinivasan and Ramakrishnan 1983). A wide variety of such materials are available to a designer. Two such classes are thermosetting polymers and thermoplastic polymers (Crawford 2006). Their initial target applications were in aerospace industry and later became viable alternative material in the sporting industry, automotive and in construction industries. Thermoplastic polymers can be re-shaped by repeated heating and cooling without losing their properties (Arzamasov (Ed), 1989, Crawford 2006). They soften on heating and become rigid on cooling. On the other hand, thermosets remain rigid during reheating till

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they are converted into char. This difference in behaviour on heating is due to the relatively weak Van der Waals forces acting between the molecules of thermoplastic polymers. On heating, the bonds between the molecules weaken substantially and the material becomes soft and yieldable. In thermosetting polymers, there are covalent cross bonds (Cross link) between molecules, in addition to Van der Waals forces. Owing to these cross bonds, a thermosetting polymer remains rigid on heating (Arzamasov (Ed), 1989).

Many thermoplastics are now accepted as engineering plastics. The term engineering plastics probably originated as a classification distinguishing those plastics that can satisfactorily substitute the metals such as Aluminum in small devices and structures requiring lower mechanical properties. (Crawford 2006). Engineering plastics are the main source for developing high performance composites which possess advantages like high stiffness, high strength to weight ratio and increased chemical and atmospheric inertness compared to conventional materials. Despite these advantages, several factors have limited the wide spread use of synthetic PMCs, some of them being their high initial material costs and adverse environmental impact (Rigoberto and Geeta 2004).

Though PMCs, have higher initial material costs, low cost ones could be developed from polymers available in the form of post-consumer waste in large quantities. A city in an emergent country with a population of three million inhabitants produces about 400 tone of plastic waste each day (Burgial et al 1994). As a consequence, municipalities are becoming concerned about a 25% increase in plastic waste generation per year while the landfill area is only increasing at a 7.5% annually. Therefore, as Scott (2000) points out, by the year 2015 there will be no disposal options for plastic waste. In the year 1997, the estimated per capita demand of plastics in India was 0.800 Kgs. which was one of the lowest in Asia (Esha Shah, Rajaram 1997). The projected demand in 2000 A.D. was 2.16 Kgs. per capita (KSSPMA 1992). A boom in the consumption of plastic in India is experienced with the economic liberalization since 1991. Plastic consumption in India has more than doubled from 0.85 million tons during 1990-91 to 1.79 million tons during 1995-96. Demand for commodity plastics is growing at the rate of 15 % per year. As per a survey conducted by the All India Plastic Manufacturers Association, the total capacity

to produce PE, PVC, PP and PS was 1.39 million MT and demand was 1.55 million MT in 1995 which has increased to 1.8-1.9 million MT for 1996-97. This is concentrated in three major sectors according to the Plast India figures: infrastructure (power, roads, bridges, telecommunications and construction) which is 30 % of the total, packaging is 25 % of the total and 24 % for agriculture and water (Nanavaty 1997). The consumption of polymers in the year 2012 in India is 9 MMT which is 10 times higher than that seen in 1990 and is estimated to grow upto 13 MMT by 2015 (Figure 1.1) (Shekhar 2012). Polymers used in packages have about 50% of share in this consumption. With such a drastic growth prevailing in the consumption of plastic, recycling the post-consumed plastics may be an essential requirement to avoid issues regarding plastic waste management and environment related issues.
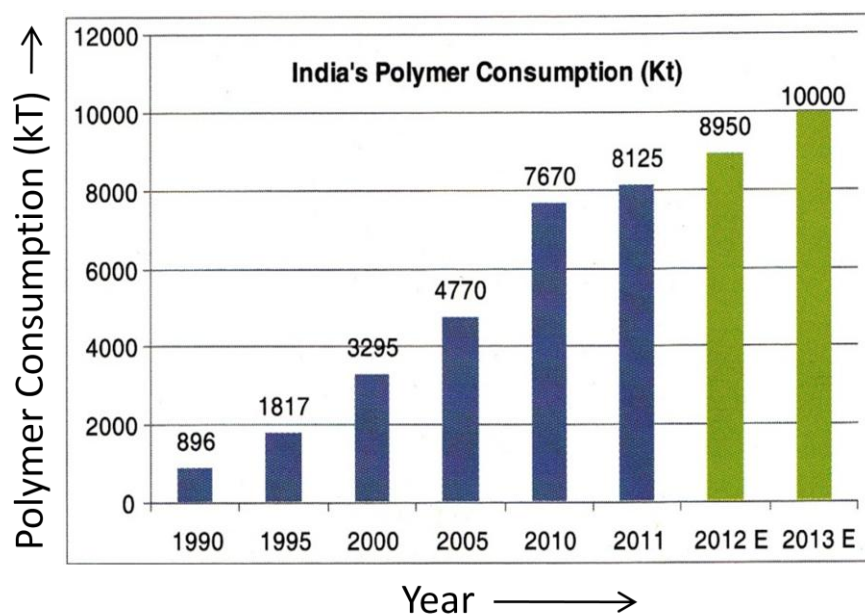
Figure 1.1: Polymer consumption in India (Shekhar 2012).

The use of recycled plastics as an alternative material has twin benefits viz. saving in cost and addressing, partially, disposal-related issues. However, mechanical properties could be lower than that of the virgin materials, but the cost effectiveness could be better. A composite made with post consumed plastics may find applications wherein no high loadings/unloading are expected (Avila and Marcos 2003).

1.3.1 Recycled thermoplastics – source of matrix materials

Although Plastics have an important place in our daily lives, their impact on the environment through all stages of their existence from manufacture till their utilization and subsequent disposal is undeniable (Sundaresan 1996). By 1990s, plastic recycling programs were common all around the world. Thermoset plastics are ground up and used as filler, and thermoplastics are either re-melted and reused or broken back down to a feedstock state. To assist recycling of plastic disposable items, the Plastic Bottle Institute of the Society of the Plastics Industry devised the now-familiar scheme of identifying plastic type. A recyclable plastic container using this scheme is marked with a triangle having three "chasing arrows" and a number enclosed, mentioning the plastic type: PETE, HDPE, PVC, LDPE, PP, PS, and others as shown in the Figure 1.2.
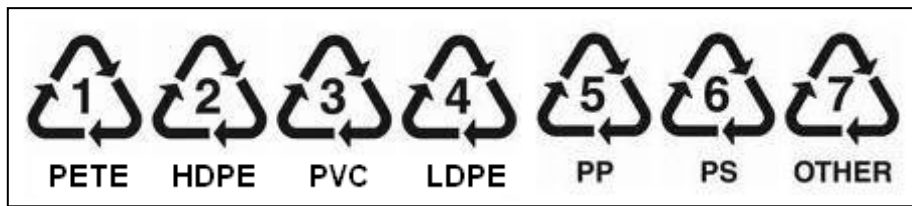
Figure 1.2: Marking scheme for recycled plastics.

Recycling plastics has many benefits; it contributes to energy savings and reduction of greenhouse gas emissions. It also saves non-renewable sources like oil and gas. Recycling also provides livelihood for millions of people and families in developing countries, either in the form of formal employment or informal economic activities. A few other advantages of recycling plastics are listed below

- Labor costs are lower - In many countries there is an existing culture of reuse and recycling, with the associated system of collection, sorting, cleaning and reuse of 'waste' or used materials.
- Transportation costs are often lower, with hand or ox carts often being used.
- Low cost raw materials give an edge in the competitive manufacturing world.
- Innovative use of scrap machinery often leads to low entry costs for processing or manufacture.

Three different approaches are suggested for recycling in the literature, they are 'biological recycling' 'energy recovery' and 'thermo-mechanical recycling' (Figure 1.3)

(Scott 2000). Biological recycling route uses the polymer biodegradation, a process dependent on the polymer type and environmental conditions. Energy recovery can be performed in two distinct ways, first by incineration where the hydrocarbon polymers replace fossil fuels and the second by pyrolysis /hydrogenation to low molecular weight hydrocarbons for use as portable fuels and polymer feedstock. Mechanical recycling is used to recover materials for reuse. Considering the costs, procedures and the environmental effects, thermo-mechanical recycling route is much preferred (Avila and Marcos 2003). This technique involves an initial process wherein the thermoplastics are granulated by extrusion followed by thermoforming.
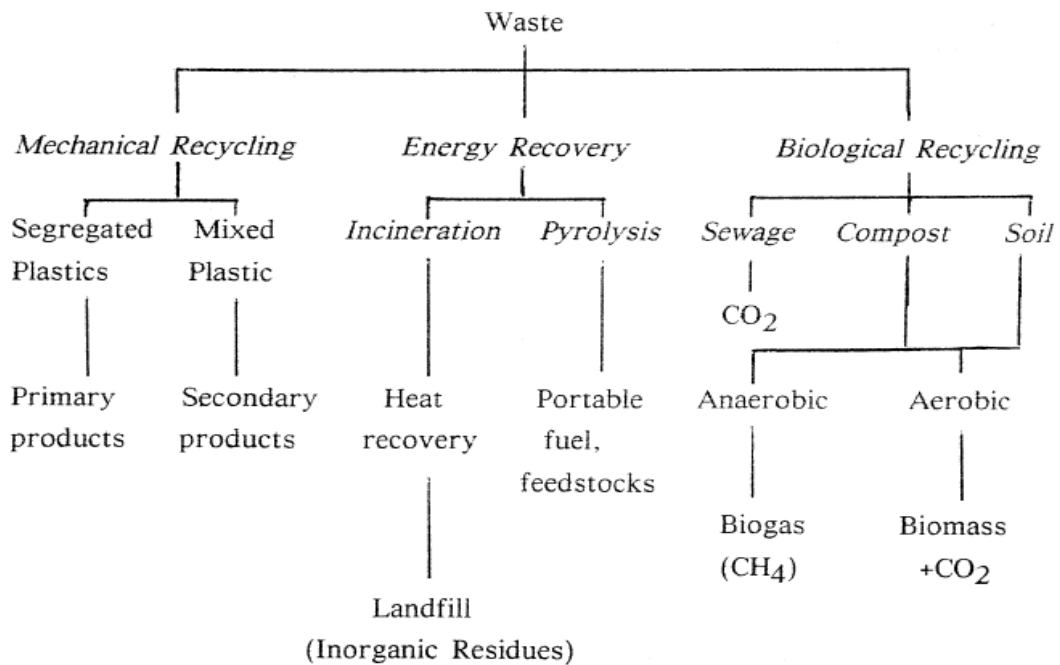
Figure 1.3: Approaches for polymer recycling (Scott 2000).

Amongst the polymers specified in the Figure 1.2, Polyethylene terephthalate is highly recyclable (code-1). It is commonly abbreviated as PET, PETE, or the obsolete PETP or PET-P, is a thermoplastic polymer resin of aromatic-aliphatic polyester family. It forms triclinic crystals with one polymer chain per unit cell. The original cell parameters were established in 1954 (Daubeny and Bunn 1954) and numerous groups have reexamined it over the years. The unit cell parameters of triclinic PET are $a = 0.444$ nm; $b = 0.591$ nm; $c = 1.067$ nm; $\alpha = 100°$; $\beta = 117°$; $\gamma = 112°$; density $= 1.52$ g/cm^3. PET consists

of polymerized units of the monomer ethylene terephthalate, with repeating $C_{10}H_8O_4$ units. PET is hard, rigid and exhibits very little wear and tear. It also has very little creep and can tolerate very high mechanical loads. The service temperature of neat polyester matrix ranges from 120 to 240 ºC. Because of its high melting points and glass transition temperature (Tg), it retains good mechanical properties at high temperatures. The chemical and solvent resistances are good (Arza Seidel, 2012). Applications of PET include gears, bearings, housings, impellers, pulleys, switch parts, bumper extensions, fibers etc. and of course PET is now renowned for its success as a replacement for glass in beverage bottles (Crawford 2002).

In 1990, the annual world production of PET fibers was about 9 million tons. The annual production of PET bottle resin in 2000 was 1.4 million ton and is growing rapidly. The majority of the world's PET production is for synthetic fibers (in excess of 60%) with bottle production accounting for about 30% of global demand. Moreover, according to Scheirs (1998), the chemical nature of PET favors a broad range of recycling options from mechanical recycling to chemical recycling. Attempts of using recycled PET (r-PET) for engineering products like bearings and gears are available in the literature (Coltelli et al. 2008, Wright and Kukureka 2001). R-PET is a desired secondary resource as the plastic is fully recyclable and may be used for manufacturing new products in many industrial areas such as packaging of detergents, cosmetics, high-quality carpets, foils, car spare parts, bearings, gears, pillow fillings for allergic persons and in fabrics. Avila (2003) reported analysis for recycled particulate composite based on dual matrix, r-PET bottles and HDPE caps of the bottles. Thermo-mechanical recycling of plastic bottle was done and their use as composite material for engineering applications was studied. Pegoretti (2004) prepared r-PET and short glass fiber composites and reported the effect of hygro-thermal aging on the molar mass and thermal properties of the composites. Avila (2005) conducted mechanical analysis on r- PET/HDPE composites by carrying out compression test and machinability evaluation. The results showed good performance for both compression and machinability. Abu-Isa et al. (1996) developed a high-impact strength PET from virgin and recycled resins by blending with co-polyester thermo-mechanical elastomer. Addition of triphenyl phosphate to polyester elastomer/PET blends encourages molecular weight buildup and improves impact strength and mechanical

properties. Verney et al. (2005) reported that weathering and recycling of PET causes degradation of polymer backbone and results in loss of polymer properties. To enhance the properties, PET was blended with polycarbonate and the blends showed better properties than neat PET. Pegoretti (2004) developed nano composites by r-PET and layered silicates. Atta (2007) developed new epoxy resin based on r-PET as organic coating. Lopez-Cuesta and Crespy (2003) reported that mechanical properties and fire resistance of r-PET was improved by using specific treatment of the waste material and incorporation of encapsulated red phosphorus in combination with co-additives.

In the plastic recycling arena, it is commonly observed that recycling process continuously degenerates the mechanical properties of the plastic. According to Pawlak et al. (2000), the unsatisfactory mechanical properties of recycled polymer are due to degradation during the reprocessing. However, amongst different plastics recycled thermo-mechanically, r-PET has displayed better retention of properties, but with little increase in brittleness (Avila 2005, Gaymans 2000). Retention of the mechanical properties even after recycling combined with its abundant availability makes r-PET a front runner as an alternative material for engineering applications. Blending r-PET for reducing brittleness and reinforcing with fillers for retaining properties though attempted in the literature (Avila and Marcos 2003), needs to be still further explored with different material combinations.

1.3.2   Polymer blends as matrix modifiers

Developing of a new composite for a specific need is a costly exercise. Polyblending is considered as an approach to economically develop new materials that are tailored for a specific performance. By definition, any physical mixture of two or more different polymers or copolymers that are not linked by covalent bonds is a polymer blend or polyblend. The properties of the resulted blend are intermediate or in some cases above the expected average properties (Margolis 2006). The concept of physically blending two or more existing polymers or copolymers to obtain products with better properties is attracting widespread interest for its commercial utilization (Mason and Sperling 1976, Utracki 1989). The first commercial blend of two dissimilar polymers was Noryl, a miscible polyblend of poly(phenylene oxide) and polystyrene, introduced by General

Electric in the 1960[s]. Since then a large variety of blends are introduced. A few such blends are Mechanical Blends, Mechano-chemical blends, Solution-cast blends, Latex blends, Chemical blends, Interpenetrating polymer networks (IPN), Semi-interpenetrating polymer networks (semi-IPN, also called pseudo-IPN), Simultaneous interpenetrating polymer networks (SIN) and Interpenetrating elastomeric networks (IEN).

Thermo-mechanical blending of recycled PET with r-HDPE by hot compression and its use for engineering applications is studied by Avila and Marcos (2003), from the point of view of stiffness and machinability. The analysis was on macro mechanical approach (Tamma and Avila 1999), with no addition of any kind of stabilizer, compatibility or additives as the objective was to develop a fully recycled material. The study concludes that addition of r-HDPE to r-PET solution reduces effective stiffness of the blend and contributes favorably to the milling operation. Although all samples underwent brittle fracture under compression, a decrease in elastic modulus and improvement in fracture strain was observed with increase in the content of r-HDPE in the blend. However, the selection of r-HDPE as a blending plastic for r-PET relied only on its availability in the form of cap of the bottle and not on the properties of material. Studies on PET based binary blend include the work of Bataille et al. (1987) who studied tensile properties and water vapor permeability of non-compatibilized PET/PP in the complete range of composition, and one composition at several compatibilizer levels. The compatibilizer was a PP–acrylic acid copolymer (PP-*g*-AA). The improvement in mechanical properties was marginal, and permeability of PP towards oxygen was reduced with the addition of PET. Sun et al. (1996) pointed out the use of acrylic acid as the active functionality of a compatibilizer has the disadvantage of being kinetically slow when esterified with the terminal OH groups of the polyester.

Besides the lower cost of the recycling, the blends can give rise to secondary materials with interesting properties. In particular, blends of polyolefins and PET can display good mechanical and permeation characteristics (Bataille et al. 1987). According to Margolis (2006), however, the most common commercial method for producing PET blend is a melt compounding process, which is simple and cost efficient. In view of vast opportunities offered by polymer blends, extensive interest is generated in research and industry to produce high quality products at low costs (Scott 2000). Regaining the

properties affected due to recycling and blending is attempted in the literature by reinforcing the matrix with fillers (Avila and Marcos 2003).

1.4   REINFORCEMENTS FOR COMPOSITES

In a broader sense, composites are the result of a combination of substantial volume fractions of high strength, high stiffness reinforcing components with a lower modulus matrix. The term "Reinforcement" is used in the mechanical load bearing sense. The use of reinforced materials in engineering applications has shown a rapid growth in the last few years. In general, composites can be classified into two groups as fiber reinforced and particle reinforced (Figure 1.4) (Agarwal and Broutman 1980).

a)   fiber reinforced composites, where the dispersed phase is fibrous with a larger length to diameter ratio.

b)   the dispersed phase for particle (or particulate) reinforced composites is equiaxed (particle dimensions are approximately the same in all directions) and include those that are spherical, rod, flake-like and with other shapes of components with roughly equal axes. It is to be noted that this characterization is incomplete if additional characteristics such as porosity are not considered. Fillers in filled systems where there may be no reinforcement at all, and where particles are used to extend the material for cost-reduction purposes, cannot be considered as particulate reinforced. The same applies for particles added for non-structural purposes, e.g., flame retarders, etc.

Fiber-reinforced composite materials consist of fibers of high strength and modulus, embedded or bonded in to a matrix with distinct interfaces (boundaries) between them. The principal fibers for commercial use are various types of glass and carbon as well as Kevlar. Other fibers, such as boron, silicon carbide, and aluminum oxide, are used in limited quantities. All these fibers can be incorporated into a matrix either in continuous lengths or in discontinuous short lengths (Mallick 2007). In many cases the cost of the resulting PMC is found to be higher owing to the material costs of the fibers (Nikhilesh et al. 2010). Particulate composites are the other important class of composites that find wide applications and have attracted industries and researchers due to their wide applications and low cost (Muhammad et al. 2011). Particulate fillers have played a vital

role in the development of commercially viable polymers. Not only do they provide significant cost reductions but certain fillers may improve processing, optical and physical properties and mechanical behaviour (Rothon 2002).
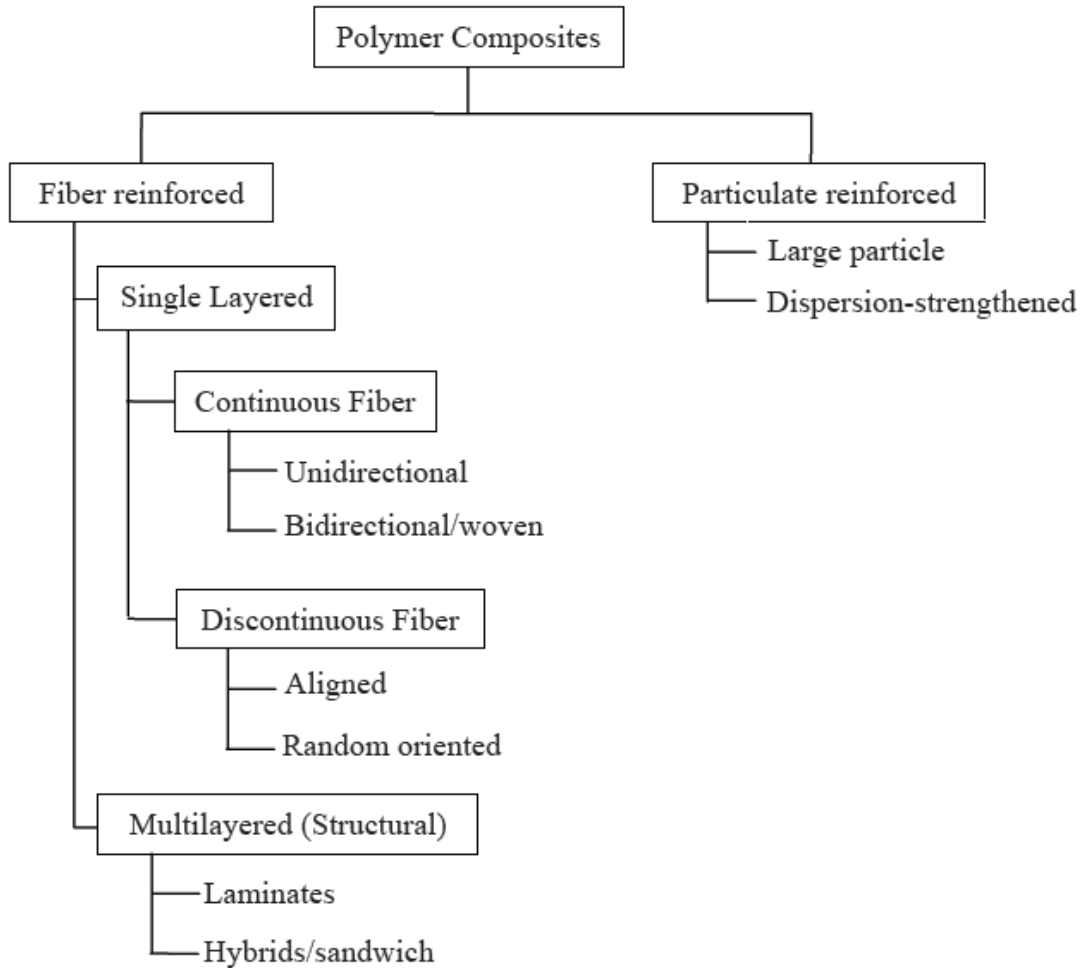
Figure 1.4: Classification of composites based on reinforcement
(Agarwal and Broutman 1980).

A variety of materials can be considered as particulate fillers for the polymers which include particles of minerals, metals, ceramics, polymers and also some industrial wastes (Shaikh and Channiwala 2006). They can be broadly classified into organic and inorganic types. Some common examples of particulate fillers are particles of alumina, silica, hollow and solid particles of glass, wood chips, fly ash (FA) and carbon black. Their classification with examples is tabulated in the Table 1.2 (Arza S (ed) Vol.10, 2012). Selection of the material largely relies on the desired properties of the composite. Further, shape of the filler particles plays an important role in determining the properties of the

composite. Hence, particulate reinforcements are normally classified based on their shapes. Spherical particulate fillers are more popular when compared to the other types.

Table 1.2: Reinforcements for polymer matrix (Arza S (ed) Vol.10, 2012).

Particulate		Fibrous	
Organic	Inorganic	Organic	Inorganic
Wood flour	Glass	Cellulose	Whiskers
Cork	Calcium carbonate	Wool	Asbestos
Nutshell	Beryllium oxide	Carbon/graphite	Glass
Starch	Iron oxide	Aramid fiber	Mineral wool
Polymers	Magnesia	Nylons	Calcium sulphate
Carbon	Magnesium carbonate	Polyesters	Potassium titanate
Proteins	Titanium dioxide		Boron
Carbon nanotube	Zinc oxide		Alumina
	Zirconia		Metals
	Hydrated alumina		
	Antimony oxide		
	Silica		
	Metal powder		
	Organo-nanoclays		
	Clays		
	Barium ferrite		
	Silicon carbide		
	Potassium titanate		

Principal advantages of spherical fillers are (Ferrigno 1978):

- Low surface area to volume ratio
- Non-scoring properties on metals
- High crush strength
- Better rheology and flow of the charge
- Regularity in shape
- Control over surface properties
- Shallow band of particle size

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Fly ash cenospheres (FAC) are the promising low cost fillers. They are one of the constituents of FA, produced during thermal power generation whose disposal is of considerable concern to ecologists (Pedlow 1978, Mohapatra and Rao 2001, Ahmaruzzaman 2010).

1.4.1 Fly ash cenospheres – material for reinforcement

Although a wide variety of reinforcements are available, from techno-economic perspective, FA cenospheres could be a better selection (Gu.J, et al 2007). The selection can further be justified if the basic aim is to address cost effectiveness of the product, saving energy and easing disposal. FAC is one such abundantly available material that can be considered as a reinforcement filler as it posses the above mentioned principal advantages. It has attracted interest lately because of the abundance in terms of volume of the material generated and the environmental linked problems in their subsequent disposal (Ferrigno 1978, Kulkarni et al. 2002). FAC are the lowest density constituents of FA which is a predominantly inorganic residue obtained from the flue gases of furnaces at pulverized coal power plants during the combustion of coal for energy production. Only 30% of FA is used by cement industry, while a large proportion often goes to landfill and ash ponds. This poses great environmental risk due to possible long term adverse effect of transition metal oxides dependent on processing condition (Alkan et.al, 1995, Ward and French 2006). Therefore, it is a great challenge to find alternative sound environmental solutions to dispose FA. Wide spread efforts, hence, are being made to develop value added products from FA (Shukla et al. (2001,2002), Aixiang et al. (2005), Dou et al. (2007)).

FAC are alumino-silicates containing approximately 52.53% SiO_2 and 30% Al_2O_3 as main constituents. The energy dispersive spectroscopy of FAC sample revealed main constituents to be silica and alumina respectively while traces of other oxides namely Fe_2O_3 and TiO_2 are also present (Narasimha Rao 1999). Compositional details of FAC particles are tabulated in Table 1.3 (Kolay 2001).

FAC being hollow spherical particles, can aid in maintaining lower density values for the composite, a feature of considerable significance in weight-specific applications (Pedlow 1978, Mohapatra and Rao 2001). Again, as the fillers are spherically shaped, the resin

spread is better and as the ashes are essentially a mixture of solid, hollow and composite particles displaying near isotropic properties, developing newer and utilitarian systems using them should be an interesting and challenging task (Kishore et al. 2002).

Table 1.3: Compositional details of fly ash cenosphere particles (Kolay 2001)

Components	Wt %	Components	Wt %
SiO_2	52.53	K_2O	1.98
Al_2O_3	30.01	MgO	0.32
Fe_2O_3	7.53	TiO_2	1.79
CaO	1.15	P_2O_5	0.45
SO_3	0.02	Loss on ignition	4.20

As these have aspect ratios closer to unity, near isotropic characteristics are displayed by them. These are inexpensive and possess good mechanical properties. When used with matrix materials, these help in reducing the cost and either retain or improve desirable and specific mechanical properties (Scheetz and Earle 1998). They possess good mechanical, rheological, electrical and thermal properties (Nath et al. 2009) and are used successfully as reinforcement for polymers in some of the reported works (Deepthi et al. 2010, Tiwari et al. 2004, OLBISI O. 1997, Domininghaus 1998, Rose and Cimino 1982). The improvement in mechanical properties certainly depends on the extent of binding between the matrix and the reinforcement. Inefficient binding leads to phase separation at the interface and loss of strength (Yang et al. 2006). In general, the interfacial interaction between the reinforcement and the matrix assumes significance in the mechanical sense as the load transfer has to be realized through these interfacial 'zones' / 'regions' (Broutman and Krock 1974).

1.5 ROLE OF INTERFACE AND ITS MODIFICATIONS

A key region that influences mechanical properties of the composite is the matrix/reinforcement interface. A series of phenomenon takes place at such interfaces. The structure of interface and the stresses generated during different stages of processing

and services have a bearing on the fracture and failure of the composite (Ranney et al. 1974). Hence it is essential to consider the interfaces in detail and examine their influence on the mechanical properties of the composite, so as to alter the properties to suit one's need in the end product. A good bonding at the interface is essential to have satisfactory load transfer from the matrix to the reinforcement. The mechanism of bonding at the interface are (Hull and Clyne 1996):

- By absorption and wetting – This mechanism prevails when one of the two bodies is in liquid phase. The adhesion is primarily due to van der Waals forces. Surface contamination, surface roughness and the relative surface energies are few influencing factors. Wetting is strongly favored if the surface energies of the two constituents are large and interfacial energy is small, as per the Dupre equation (Hull and Clyne 1996). Complete wetting is expected if the contact angle is low and the surface energy of the solid is equal to or greater than the sum of the liquid surface energy and the interface energy. A situation where the surface energy of the reinforcement exceeds that of the matrix material is likely to result in good wetting.

- By interdiffusion and chemical reaction – In this mechanism the adhesion is promoted by diffusional process or chemical reaction like in a polymer surface pair, the adhesion may be due to chain entanglements.

- Electrostatic attraction – If the interaction surfaces carry net opposite electrical charges an adhesion force may result.

- Mechanical keying – there can be an improvement in bonding by locking of asperities on the interacting surfaces.

- Residual stresses – presence of residual stresses also influences the nature of interfacial contact.

The interfacial characteristics can be modified in a number of ways, a popular one being the chemical treatment. Reinforcing materials such as FAC contain oxides like Al_2O_3, SiO_2 and Fe_2O_3 which form links to hydroxyl groups during their contact with atmospheric moisture and convert into water molecule. The presence of water, additionally, reduces the wettability of the reinforcement as it lowers the surface energy.

Coatings that function as coupling agents hence are expected to raise the effective surface energy of the reinforcement. The coupling agents primarily provide a chemical link between the oxide groups on the fiber surface and the polymer molecule of the thermoplastic.

The silane coupling agents have a general formula $R-Si-X_3$ wherein this multifunctional molecule reacts at one end with the surface of the filler and at the other with the polymer phase. The X group in these is a hydrolysable one and hence the silane is hydrolyzed to corresponding silanol (R-OH) in the presence of aqueous solution. These silanol molecules compete with water molecules to form hydrogen bonds with the hydroxyl groups bound to the reinforcement surface (Hull and Clyne 1996). When the reinforcement is dried, the free water is driven off and the condensation reaction then occurs, both at silanol/surface junction and between neighboring silanol molecules. The result is a polysiloxane $(X-R-Si(OH)_3)$ layer bonded to the filler/reinforcing surface presenting an array of R functional groups to the environment. These open functional groups involve in curing reaction with the matrix polymer and establish a bond (Hull and Clyne 1996). Besides improving the bonding and the mechanical properties, the coupling enhances the electrical, thermal and magnetic properties due to increased effective contact at the interface. Another important feature is the increased resistance to environmental effects. The bonding also serves to reduce the effect of hostile environments at the reinforcement causing degradation and thus retains useful mechanical properties of the composite in spite of its exposure to such environments. Silane treatments help in better wetting while those wherein dirt or greasy/oily layers envelope the fillers, the effectiveness of the medium to wet reinforcements/fillers reduces (Farinha et al 2000). Their presence also affects the properties including the mechanical behaviour. The mechanical properties of polymer-FAC composite is inferior owing to poor interfacial interactions between the hydrophilic FAC surface and hydrophobic polymer (Guhanathan et al. 2001). However, surface treated FAC is found to improve the interfacial interactions (Thongsang and Sombatsompap 2006). A mechanism of interaction between Silane-69 (Bis(3-triethoxy silyl) propyl tetrasulfide) coupling agent and FA, as explained by Nabil et al. (2004), is shown in the Figure 1.5.
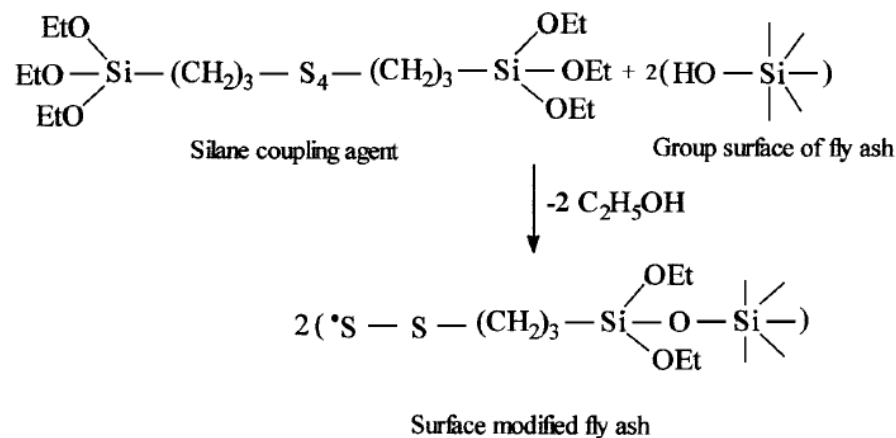
Figure 1.5: Reaction between Silane-69 coupling agent and fly ash

Mechanical and morphological properties of recycled HDPE filled with Calcium Carbonate and FA were investigated by Atikhler et al. (2006). Authors investigated the effect of surface treated FA on the mechanical properties of HDPE as compared to conventional calcium carbonate filler. FA was subjected to surface treatment with 3-amino propyl triethoxy silane. Tensile strength slightly increased on addition of FA as filler when compared to conventional calcium carbonate. However, higher increase was noticed when modified FA was used especially, up to 30% of filler content. The decrease in elongation at break was higher for ash filled composites when compared to calcium carbonate filled composites. This decrease in property was higher when treated- FA was used as filler. SEM results showed a good interfacial adhesion between ash and HDPE matrix. Authors concluded that ash is a good replacement for calcium carbonate. Further, no compatibilizers were used and also thermal characterization of the composites was not done.

Effect of surface coverage of silane treated CaCO3 on the tensile properties of polypropylene composites are analyzed by Demje´n and Puka´nszky (2004). Amino functional silanes showed a strong reactive coupling effect leading to a maximum tensile strength (Phueakbuakao 2008). Effect of silane and zirconate coupling agents on mechanical properties of mica/epoxy composites is studied by Bajaj et al.(1992). They showed that the tensile modulus and flexural strength values are improved by the surface treatment of the coupling agents. Mathew et al. (2004) reported that properties of silica-filled styrene-butadiene rubber composites were improved through plasma surface

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modification of silica. The filler dispersion, as revealed by scanning electron microscopy, was found to be greatly improved by the plasma as well as silane treatment. Kulkarni and Kishore (2002) reported that the FA filled epoxy composite showed improved compression strength after exposure to aqueous media but the surface treated FA particles in epoxy showed reduction in compression strength. Ramakrishna et al. (2006) concluded that the toughened epoxy with FA composites showed improved compressive and impact strength. However, the tensile strength decreased and the tensile modulus increased with increase in FA content in epoxy (Srivastva and Shembekar 1990). Since cenospheres are microsized hollow spheres they give rise to a composite which have very fine pores of micron size which absorb greater impact energy and increases the impact strength of the composite (Ferreira and Capela 2010).

A study on FA filler of varying sizes as reinforcement in waste PET polymeric materials is conducted by Seena et al. (2010). The effect of filler size, filler weight percentage, and silane coupling agent (3-aminopropyltrimethoxysilane and vinyltrimethoxy silane) on tensile, flexural, and impact properties of the composites is analyzed. The dispersion of filler in the matrix and filler/matrix interaction has been analyzed by scanning electron microscopy. The authors reported that FA is good filler for r-PET polymer matrix. Smaller FA particles impart higher tensile strength with an increase in FA content in comparison to larger ones. The tensile and flexural strength increased up to 15% loading for all particle sizes and then decreased due to filler agglomerations at higher filler contents. The impact strength of r-PET is reported to have a sharp decrease with FA as filler irrespective of its size. The elongation value of the composites also showed that the brittleness of the r-PET increases on adding FA particles. Agglomeration of fillers at higher filler contents is observed from SEM photos. It was also found that both amino silane and vinyl silane coupling agents cause an increase in the tensile strength and flexural strength of composites due to their improved interfacial interaction. They observed that elongation value increases drastically with addition of FA treated with coupling agent. Agglomeration is lower in the presence of coupling agents. Impact resistance of low-impact FA/PET composites could be improved by silane coupling agents. Scanning electron micrographs of silane treated and untreated composites showed improved FA-PET interaction by silane coupling agent. Further, 3-aminopropyl

trimethoxy silane was observed to provide better tensile strength and impact resistance at 1% concentration when compared to vinyltrimethoxy silane which inturn was found to be better at 1% concentration for elongation (Seena et al. 2010). As observed by Suresha et al. (DOI 10.1002/pc.20380), there are only a few studies on tribological characterization of hollow microspheres filled polymer composites available. Added to that, studies on treated cenospheres filled polymer composites are rare (Suresha et al. 2010). R-PET reinforced with treated FAC can help improve the properties of the composite. The materials being from the recycled arena could produce low cost products. Development of suitable process and its optimization is required to reduce the cost of the product. Generic processes composites and their implications are described below.

1.6 PROCESSING OF COMPOSITES

Processing is the science of transforming materials from one shape into another. Every material possesses unique physical, mechanical and processing characteristics and hence a suitable manufacturing technique must be selected to transform the material to its final shape. In the last half of the twentieth century, the processes used for fabrication of parts made from composite materials evolved from operations relying on manual labor to manufacture by automated equipment controlled from sophisticated microprocessor systems. Early pioneers combined raw materials and formed the final structure by hand lay-up or spray-up on open molds. The parts were cured at ambient temperature. As the advantages of PMC's are felt, these synthetic materials began to penetrate virtually every other market worldwide, from automotive and marine to primary structural elements of aircraft and bridges. Such widespread growth in product applications mandated corresponding growth in materials technology, design approaches, and fabrication processes (Arza Seidel (ed) Vol.2, 2012). Some of the fabrication processes widely practiced on the shop floor include open mould processes like hand layup, autoclave, press cure oven cure process etc. the closed mould processes include compression moulding, injection moulding transfer moulding thermo-stamping etc. Some of the processing options for thermoset and thermoplastic materials with variety of reinforcement are given in the Figure 1.6 (Reinhart 1998).

Injection Moulding and Compression Moulding are the two moulding processes that are very widely practiced on the shop floor, in the manufacture of polymer components. Compression moulding is the oldest processing method for manufacturing plastic parts. It is a high volume, high pressure method using pressure and heat to shape the plastic in a mould. It is a cheap and fast process for producing medium strength components. Being suitable for small to medium sized components, the process facilitates the production of simple and complex shapes (Sanjay Mazumdar 2002).
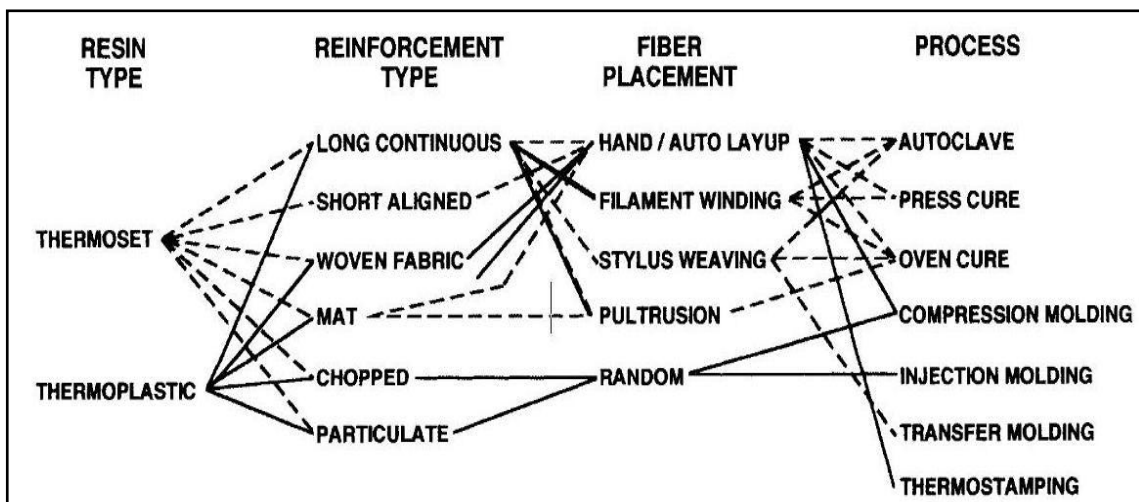
Figure 1.6: Constituents of PMCs and manufacturing options (Reinhart 1998).

1.6.1 Compression moulding

Compression moulding is a cost effective process when compared to the injection moulding and stamping. It is the oldest and unique process for moulding of plastic components that produce parts of near net shape. The components of a compression moulding machine is shown in the Figure 1.7. Compression-moulding equipment consists of a matched mould, a means for heating the plastic and the mould, and some method for exerting force on the mould halves. For severe moulding conditions, moulds are usually made of various grades of tool steel (Manas and Salil 2006). Many are polished to improve material flow and overall part quality. Brass, mild steel or plastics are used as mould materials for less severe moulding conditions or short-run products. In compression moulding, a pressure of 160 kg/cm^2–210kg/cm^2 is suitable for phenolic materials. The lower pressure is adequate only for an easy-flow material and a simple

uncomplicated shallow moulded shape. For a medium-flow material with average-sized recesses, cores, shapes, and pins in the moulding cavity, a pressure of 210 kg/cm^2 or above is required.
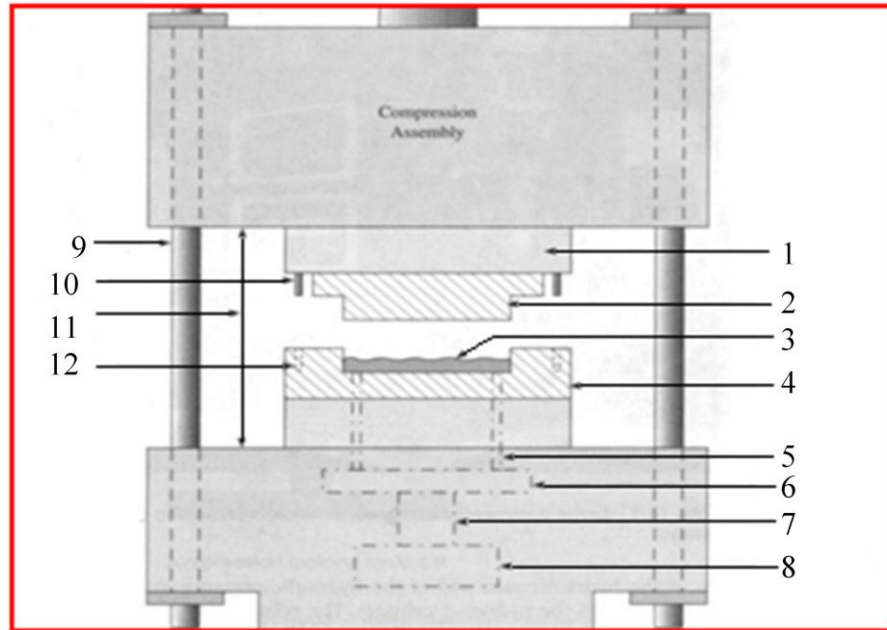
Part No.	Description	Part No.	Description
1	Heated Platen	7	Hydraulic Piston
2	Male Mould	8	Hydraulic Unit
3	Material Charge	9	Slide Rod
4	Female Mould	10	Daylight Opening
5	Ejector Pin	11	Guide Pin
6	Knockout Plate	12	Guide Hole

Figure 1.7: Components of compression moulding machine.

Compression moulding optimized for recycled material could aid in reducing total cost of the product. In this method of moulding, the plastic in the form of powder, pellet or disc is dried by heating and then further heated close to the curing temperature; the heated

charge is then loaded directly into the mould cavity. The temperature of the mould cavity is held at 150˚C–200˚C, depending on the material. The mould is then partially closed, and the plastic, which is liquefied by the heat and the exerted pressure, flows into the recess of the mould. At this stage, the mould is fully closed, and the flow and cure of the plastic are complete. Finally, the mould is opened, and the completely cured moulded part is ejected. The stages of compression moulding are shown in the Figure 1.8.
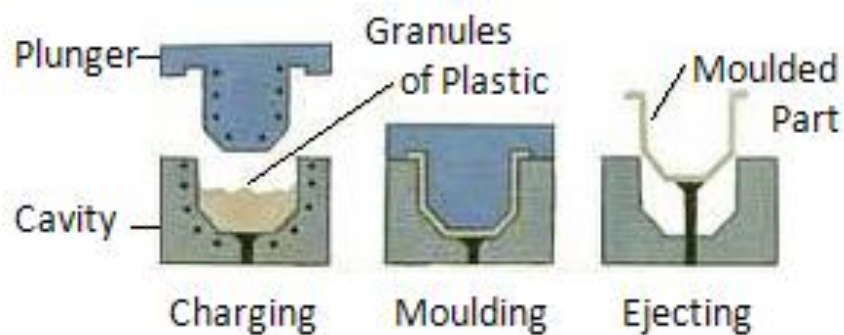
Figure 1.8: Stages of compression moulding.

In compression moulding of thermosets, the mould remains hot throughout the cycle. As soon as a moulded part is ejected, a new charge of moulding powder can be introduced. On the other hand, unlike thermosets, thermoplastics must be cooled to harden. So before a moulded part is ejected, the entire mould is cooled, and hence, the process is time consuming for thermoplastics. Although compression moulding is commonly used for thermosetting plastics, in special cases, such as when extreme accuracy is needed, thermoplastics are also compression moulded. Like the moulding process itself, compression moulding machinery is relatively simple. Most compression presses consist of two platens that close together, applying heat and pressure to the material inside a mould. The majority of the presses are hydraulically operated with platens ranging in size from 39 to 7,200 cm^2 or more. The platens exert pressures ranging from 6 to 10,000 tons. Compression moulds can be divided into hand moulds, semiautomatic moulds, and automatic moulds. The design of any of these moulds must allow venting to facilitate escape of steam, gas, or air produced during the operation. After the initial application of pressure, it is a common practice to open the mould slightly to release the gases. This procedure is known as breathing (Manas and Salil 2006).

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1.6.2 Moulds for compression moulding

Hand moulds are used for experimental runs, for a small production of items, or for moulding articles of complex shape that requires dismantling of mould sections to release them. Semiautomatic moulds consist of plunger and cavity halves mounted firmly on the top and bottom platens of the press. The operation of the press closes and opens the mould and actuates the ejector system for removal of the moulded article. However, an operator must load the moulding material, actuate press controls for the moulding sequence, and remove the ejected piece from the mould. This method is widely used. Fully automatic moulds are specially designed for adaptation to a completely automatic press. The entire operation cycle, including loading and unloading of the mould is performed automatically, and all moulding operations are accurately controlled. Tooling must be of the highest standard to meet the exact demands of high-speed production. Automatic moulds offer the most economical method for long production runs due to low labor costs. The three common types of mould designs are open flash, fully positive, and semi positive as shown in the Figure 1.9.
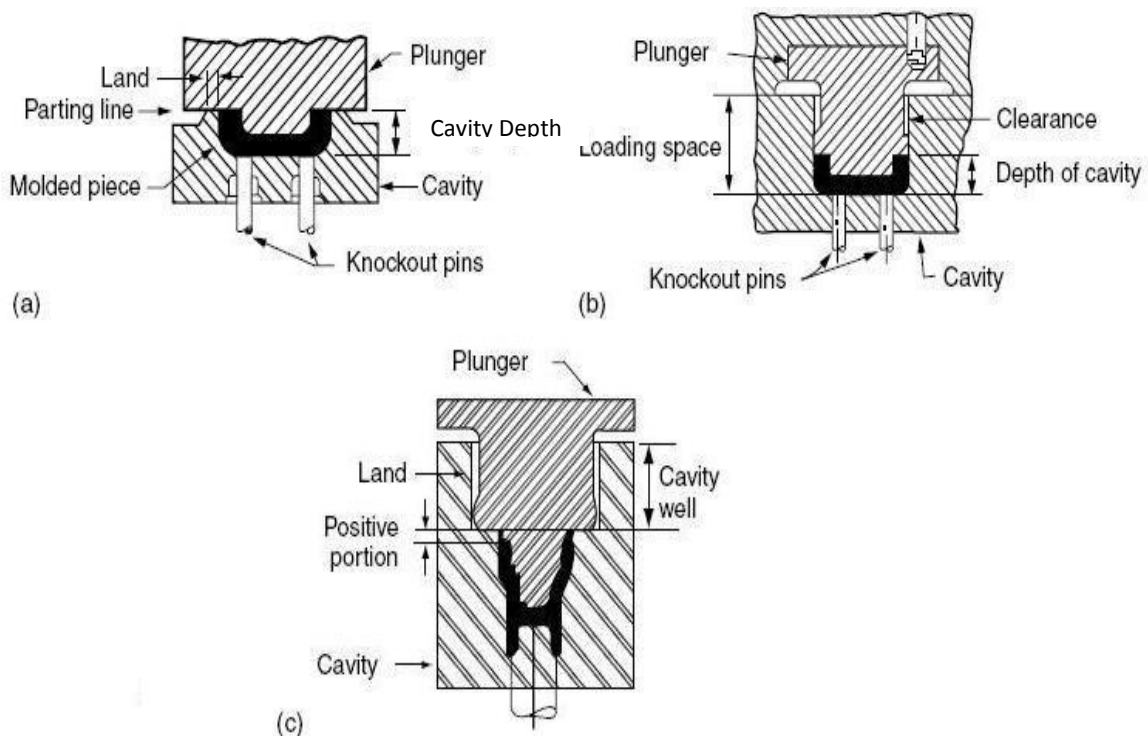
Figure 1.9: Types of moulds for Compression moulding (Vaill, 1962).

A. Open Flash

In an open flash mould (Figure 1.9 a) a slight excess of moulding powder is loaded into the mould cavity (Vaill, 1962). On closing the top and bottom platens, the excess material is forced out and flash is formed. The flash blocks the plastic inside the cavity and causes the mould plunger to exert pressure on it. Gas or air may get trapped during a quick closure of the mould and finely powdered material may splash out of the mould. However, careful closing of the mould gives very good results (Vaill, 1962). This method is often selected for moulding materials with high melt viscosities. Since most rubbers have high melt viscosities, the flash mould is widely used for producing gaskets and grommets, tub and flash stoppers, shoe heels, door mats, and many other items. Because of lower pressure exerted on the plastic in the flash moulds, the moulded products are usually less dense than when made using other moulds. Moreover, because of the excess material loading needed, this process results in wastage of raw materials. However, the process has an advantage of cheap moulds and low labor costs needed for weighing out the powder.

B. Fully Positive

In the fully positive moulds (Figure 1.9 b) no allowance is made for placing excess powder in the cavity (Vaill, 1962). If excess powder is loaded, the mould will not close; an insufficient charge will result in reduced thickness of the moulded article. One major drawback of positive mould is that it requires accurately measured charge. Another disadvantage is that the gases liberated during the chemical curing reaction are trapped inside and may show as blisters on the moulded surface. Excessive wear of the sliding fit surface and difficulty in ejecting the moulding are other reasons for discarding this type of mould. The mould is used on a small scale for moulding thermosets, laminated plastics, and certain rubber components.

C. Semipositive

The semipositive mould (Figure 1.9 c) combines certain features of the open flash and fully positive moulds and makes allowance for excess powder and flash (Vaill, 1962). It is also possible to obtain both horizontal and vertical flash. Semipositive moulds are expensive to manufacture and maintain when compared to other types, but they are much better from an applications point of view. Satisfactory operation of semipositive moulds

is obtained by having clearance (0.025/25 mm of diameter) between the plunger (top force) and the cavity. Moreover, the mould is given a 2–38 taper on each side. This allows the flash to flow on and the entrapped gases to escape along with it, thereby producing a clean, blemish-free mould component.

The design of compression moulding process is based on the trial and error method, which is a very expensive and time consuming process. In this regard, adapting one of the available quality improvement philosophies is very essential. Some of these methods are Total Quality Management (TQM), Lean method, Fishers method, Factorial design, Response surface method, Mixture design, Six Sigma method, Taguchi design etc. Amongst these TQM and Six Sigma method are the two widely adapted philosophies (Baird and Craig 2011). However, Six Sigma philosophy is considered to be a better option due to its concerns for improving customer satisfaction, shortening cycle time and lowering defects along with embedded awareness of quality in all organizational process, proposed by TQM (Pande et al. 2000).

1.7 SIX SIGMA METHODOLOGIES FOR EXPERIMENTAL ANALYSIS OF THE COMPOSITES

The Six Sigma provides two methodologies, one for optimizing existing processes and the other for new product/process designs (Joseph and William 2005). DMAIC (Define, Measure, Analyze, Improve and Control) is useful in optimizing existing processes and DMADV approach (Define, Measure, Analyze, Design and Verify) for new product/process development (Koning and Mast 2004). Systematic and disciplined implementation of these methodologies ensures that the causes of defects are found and later eliminated by focusing on process outcomes that are of critical importance to the quality. Tables 1.4 and 1.5, delineates the generic flow of the DMAIC and DMADV approaches respectively. Further, the use of design of experiments (DOE) method makes the adaptation of Six Sigma much easier. DOE is a structured and organized method to determine the relationship between two or more factors affecting a process and its output (Baird and Craig 2011). Establishing such relations is very essential for achieving the objectives of Six Sigma.

1.8   DESIGN OF EXPERIMENTS APPROACH (DOE)

Production at highest level involves precise control over the operational parameters concerning production rates and quality. An effective production practice must have precise analysis and control of the operational parameters for obtaining rejection free, quality product. This is achieved by developing a robust process independent of external variables and then appropriate conclusions can be drawn. A scientific approach to develop robust process is to use statistical Design of Experiments (DOE) which refers to the process of planning the experiment so that appropriate data that can be analyzed by statistical methods is collected, analyzed and concluded into results. When a given problem involves data that are subjected to experimental errors, statistical methodology is the only approach for analysis (Douglas and Montgomery 2001).

Table 1.4: Generic flow of DMAIC approach in Six-Sigma (Sahoo et al. 2008)

Phase	Steps
Define	Identify and map relevant process. Identify targeted stakeholder. Determine and prioritize customer needs and requirements. Make a business case for the project.
Measure	Select one or more parameters critical to quality (CTQ) functions. Determine operational definitions. Assess the current process capability. Define objectives.
Analyze	Identify potential influence factors. Select the vital few influence factors.
Improve	Quantify relationship between control factors and CTQs. Design actions to modify the process or settings of influence factors in such a way that the CTQs are optimized. Conduct pilot test of improvement actions.
Control	Determine the new process capability. Implement control plans.

Table 1.5: Generic flow of DMADV approach in Six-Sigma

Phase	Steps
Define	Decide goals that are consistent with customer demands and the enterprise strategy.
Measure	Measure and identify CTQs (characteristics that are Critical To Quality), product capabilities, production process capability, and risks.
Analyze	Analyze to develop and design alternatives, create a high-level design and evaluate design capability to select the best design.
Design	Design details, optimize the design, and plan for design verification.
Verify	Verify the design, set up pilot runs, implement the production process and hand it over to the process owners.

1.8.1 Taguchi's DOE approach.

The classical DOE methodology, which was largely motivated by programs to increase agricultural production was postulated by Sir R.A. Fisher. This technique was the first to propose the conditions for experiments involving multiple factors. The Fisher's method is popularly known as factorial design of experiments. A full factorial design considers all possible combinations for a given set of factors at more than one level. This method is suitable when only few factors are to be investigated and becomes deplorable for multiple factors. Since many industrial experiments usually involve a significant number of factors, a full factorial design results in a large number of experiments. Taguchi method, developed by Genichi Taguchi (1990), is one of the technique for optimizing a process or design using multiple input parameters. Cesarone (2001) gives a basic outline of areas in which full factorial and Taguchi's methods differ (Table 1.6). Due to these differences, Cesarone recommends determining an ideal method for the study on a case-by-case basis, and to adapt features of each technique if necessary. Taguchi's method, combines the experiment design theory and the quality loss function concept, is used in developing robust designs for products, processes and in solving some confusing problems of manufacturing (Tsao and Hocheng 2004).

The complete Taguchi's method comprises of three main phases, all intended to be conducted offline. These three phases include system design, parameter design, and tolerance design. Taguchi parameter design stage commonly referred to as the Taguchi method is the phase used in this study. This phase requires known factors and the production is in progress. The major goal of this phase is to increase the performance of the production process by adjusting the factors, critical to quality (Roy 2001). The major goal of this phase is to increase the performance of the production process by adjusting the controllable factors.

Taguchi's method of experimental design is a viable methodology which not only provides maximum amount of information with minimum number of trials but also establishes functional relationships between the input and output variables (Syrcos 2003). Taguchi method used by Vernon and Ozel (2003) to establish correlation between turning parameters and surface roughness is found to be very successful. This statistical method was initially developed by Taguchi to improve the quality of manufactured goods, in Japanese industries and since then it is receiving huge attention in the U.S.A and worldwide. Taguchi methodology pushes quality back to the process design stage prior to the manufacture of the product to reduce the variability of product quality caused due to the process variations. Consequently rejections, inspection costs and warranty claims are reduced. One of the major advantages of using Taguchi approach is the use of orthogonal arrays (OA) (Taguchi and Konishi 1987) to minimize the number of experimental trials thus reducing time and material cost. The real power of using OA is its ability to evaluate several factors simultaneously with minimum number of tests (Phillip and Ross 2005). Table 1.7 shows number of factors, levels and trials supported by each OAs.

While there are many standard orthogonal arrays available, each of the arrays is meant for a specific number of independent variables and levels. L4, L8, L12, L16 and L32 are two levels OAs where as L9, L18 and L27 are three levels OAs (Phillip and Ross 2005). The most common OAs used are L4, L8, L9 and L27. Further filtration of the OA in the group is based on the total Degrees Of Freedom (DOF) of the variables used in the experiment and that available with the OA. The degree of freedom refers to the total

Table 1.6: Comparison of Taguchi method with DOE method (Cesarone 2001)

Factor	DOE method	Taguchi method
Process knowledge	Assumes no fundamental understanding of the process being investigated	Requires knowledge of the process and the interactions likely to exist between inputs
Number of tests	Requires all combinations of inputs	Requires a much smaller number of combinations
Noise factors	Traditionally ignores noise factors, but they can be added to the plan (which cause the number of tests to multiply)	Includes the noise factors in the design
Variability Ignores	variability and assumes a deterministic nature of the system to find the most effective combinations of inputs to maximize or minimize output	Assumes a stochastic system, looking at both levels and variability of the output to allow the selection of input variable combinations to optimize output or minimize variability
Confirming experiment	Does not require a confirming experiment, since all input combinations were tested	Should include a confirming experiment, because the selected input combinations were probably not part of the original experimental plan

Table 1.7: Comparison between OA and Full factorial designs in terms of number of trials for experiments (Phillip and Ross 2005).

Orthogonal Array	No. of Factors	No. of Levels	No. of Trials (OA)	No. of Trials (Full Factorial)
$L_4 (2^3)$	3	2	4	8
$L_8 (2^7)$	7	2	8	128
$L_9 (3^4)$	4	3	9	81
$L_{12} (2^{11})$	11	2	12	2048
$L_{16} (2^{15})$	15	2	16	32768
$L_{16} (4^5)$	5	4	16	1024
$L_{18} (3^7)$	7	3	18	2187
$L_{27} (3^{13})$	13	3	27	1594323

number of independent comparisons made with the data. For an experiment involving more than one parameter, the DOF is calculated using the equation 1.1 (Aminoiiah et al. 2007). A parameter at three levels a, b and c can have two independent comparisons namely the first between a and b and the second between b and c, i.e., DOF is two.

$$DOF = (\text{no. of factor levels} - 1) \times (\text{no. of factors}) \qquad 1.1$$

An experiment conducted to understand the influence of 4 independent variables with each considered at 3 levels need to use L9 OA. A L9 (3^4) OA has 4 columns for the variables and 9 rows giving the parameter setting for 9 experiments to be conducted. The total DOF of the L9 array, hence, is number of experiments-1, i.e., 9-1=8. This means that L9 OA can be used for an experiment having maximum DOF of 8. The experiment having 4 independent variables at 3 level has 4*(3-1) = 8 DOF. This array however assumes no interactions between parameters. For considering the interactions between the parameters, an OA of higher degree of freedom must be considered.

1.8.2 Steps involved in Taguchi's method

The implementation of Taguchi's method involves following major steps

1.   Identify the factors/interactions.
2.   Identify the level of each factor
3.   Select an appropriate Orthogonal Array (OA)
4.   Assign the factors/interactions to the column of OA
5.   Conduct the experiments
6.   Analyze the data and determine the optimal levels and
7.   Conduct the confirmation experiment.

 The details of the above steps are discussed below

1. Identify the factors/interactions

It is important to gather knowledge on the factors that are likely to influence the outcome of the process. Pilot experiments can be conducted to decide on this issue or discussions with the people involved in the project may be helpful in compiling a comprehensive list of factors.

2. Identify the level of each factor

The number of levels for each variable is decided after the selection of independent variables. The selection of number of levels depends on the effect of the level setting on the performance of the parameters. Using the parameters and their levels, Ishikawa diagrams is drawn for better understanding of the experimentation. Ishikawa diagrams (also called fishbone diagrams, cause and effect diagrams or Fishikawa diagrams) created by Kaoru Ishikawa in 1990 are the graphical representations that show the causes of a certain event (Ishikawa and Kaoru 1990).

3. Select an appropriate Orthogonal Array

On fixing the number of independent variables, their levels and interactions, the total degree of freedom can be evaluated. A study that involves five factors at three levels and three interactions has 22 ((5*2) + (3*4)) DOFs. The smallest OA that provides minimum 22 degree of freedom is L_{27} (3^{13}) with 26 degree of freedom, hence is the selection. The combinations of variables and their levels in the form of OA are often available in most of the doe text books. The interactions between the variables are normally selected from the linear graph of the OA (Phillip and Ross 2005).

4. Assign the factors/interactions to the column of OA

The assignment of the independent variables to the different columns of OA is very essential. Such assignments are usually done with reference to the OA factor assignment tables. In case of mixed level variables and interactions between variables, an interaction table of corresponding OA is referred. Finally, before conducting the experiments, the actual level values of each design variable shall be decided. It is to be noted that the significance and the percentage contribution of the variables changes depending on the level values assigned. It is the designers' responsibility to set proper level values from previous experience.

5. Conduct the experiments

Experiments can then be conducted with reference to the combinations of parametric levels, as specified by the OA. It is essential to conduct all the experiments specified in the OA randomly. The interaction and dummy columns shall not be considered during

experimentation. These columns however are needed while analyzing the response to understand the interaction effects. The performance parameter shall also be noted down for each experiment to conduct sensitivity test.

6. Analyze the data and determine the optimal levels

The most common statistical technique to determine the influence of the factor levels on the response variable is analysis of variance (ANOVA) (Christopher 2003), Like any other statistical procedures, the analysis of variance has three assumptions. Technically, these assumptions should be satisfied for the validity of ANOVA procedure. These assumptions are (Minitab 2001)

1. The observations at each factor level should be independent of each other.
2. The population variances at each of the factor levels must be same.
3. The observations of each factor level should follow a normal distribution.

A random selection of observations ensures satisfaction of the first assumption. Bartlett's test and Levene's test are the tests available to validate the equality of population variances. Bartlett's test assumes that the observations are obtained from a normal distribution; whereas, Levene's test does not require normality (Christopher 2003). An experiment with the test p-values evaluating, lower than reasonable error rate (say 5%), suggests that the population variances are the same at each of the factor levels. The third assumption is checked using a plot which is referred to as a normal probability plot. The observations in this plot must be a straight line for the validity of the third assumption. Since each experiment is a combination of different factor levels, it is essential to segregate the individual effect of independent variables. This can be done by evaluating the mean value of each level of a particular independent variable. This is done by summing up the response values for corresponding level settings. The sum of squares is then calculated by using the equation (1.2).

Sum of squares for parameter A:

$$\mathbf{SS_A = (\Sigma A_i{}^2/n_{Ai}) - T^2/N} \tag{1.2}$$

Where,

A_i = sum of observations under A_i level,

n_{Ai} = number of observations under A_i level

T = sum of all observations

N = total number of observations

From Sum of square Mean square value is calculated using the equation 1.3

$$\textbf{Mean Square for A: } MS_A = SS_A/DOF \tag{1.3}$$

Where,

SS_A = sum of squares for parameter A

DOF = degree of freedom of parameter A

The F ratio is calculated using the equation (1.4)

$$\textbf{F ratio for A} = MS_A /MS_{error} \tag{1.4}$$

Where,

MS_{error} = Mean square for error (unspecified columns)

Finally the percentage contribution of each parameter is calculated using the equation (1.5)

$$\textbf{Percentage Contribution} = SS'_A * 100 / SS_T \tag{1.5}$$

Where,

$$SS'_A = SS_A - [MS_E * DOF_A] \tag{1.6}$$

7. Conduct the confirmation experiment

A confirmation experiment is the final step in the DOE process. The purpose of such an experiment is to validate the conclusions drawn during the analysis phase. This is unnecessary if full factorial experiments are conducted. However, they are particularly important when screening, low resolution, small fractional factorial experiments are conducted owing to confounding within the columns of OA. The process involves

- Identification of statistically significant factors and levels from a technical viewpoint.
- Identification of statistically insignificant factors and the levels that is most economical.
- The test is performed by using a specific combination of statistically significant factors and levels previously evaluated.

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1.8.3 Process optimization

The main cause of poor yield in manufacturing processes is the variations in the process parameters. These sources of variation (noise) are the variables that are either controllable or expensive or impossible to control. Process optimization is not meant for the parameter settings of uncontrollable noise variables rather they are meant for determining the parameter settings for controllable design variables. To attain this objective, the control parameters, also known as inner array variables, are systematically varied as stipulated by the inner OA. Every experimenter must plan ahead and conduct experiments to obtain sufficient relevant data so that he can infer the reasons behind the observed phenomenon. It can be done so by Taguchi Method that treats optimization problem in two categories.

1. Static Problems

In general, a process has several control factors that directly decide the target or desired value of the output. The optimization then involves determining the best control factor levels so that output is at the target value. Such a problem is called a "static problem". The P-Diagram (Process/Product diagram) for static problems is shown in Figure 1.10.
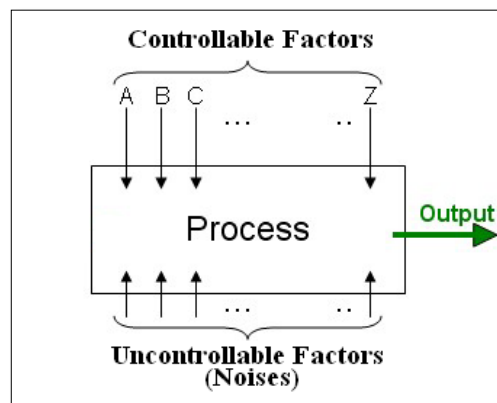
Figure 1.10: P-Diagram for static problems (Minitab 2001)

Although noises are shown in the P-Diagram, it has no effect on the output. This is the primary aim of the Taguchi experiments – to minimize variations in the output in presence of noises in the process. The process is then said to be ROBUST. Depending on the type of characteristic being evaluated, there are three S/N ratios (ratio of mean to variance) of interest for optimizing a static problem.

A. **Lower is better:** This is usually chosen for all undesired characteristic like "defects". The characteristics could be residual stress, cracks, blow holes etc. To calculate S/N ratio for such characteristics, the equation used is

Where

   r is number of repetitions in a trial

   y_i is the response.

B. **Higher is better:** This is usually chosen for all desired characteristics. It is useful when the response parameter should have larger value to achieve good performance. The characteristics could be strength, material utilization, efficiency etc. To calculate S/N ratio for such characteristics, the equation used is

C. **Nominal is better:** This is usually chosen when the response parameter is most desired i.e., neither a small value nor large. To calculate S/N ratio for such characteristics, the equation used is

Where

   V_m is the variance due to mean and V_e is the variance due to error.

2. Dynamic Problems

If a given process has a signal input that directly determines the output, the optimization involves determining the best control factor levels so that "input signal/output" ratio is closest to the desired relationship. Such a problem is called as a "dynamic problem". This is best explained by a P-Diagram which is shown in Figure 1.11. In this case, the primary aim of the Taguchi experiments is to minimize variations in the output inspite of the presence of noise in the process. This is achieved by getting improved linearity in the input/output relationship.
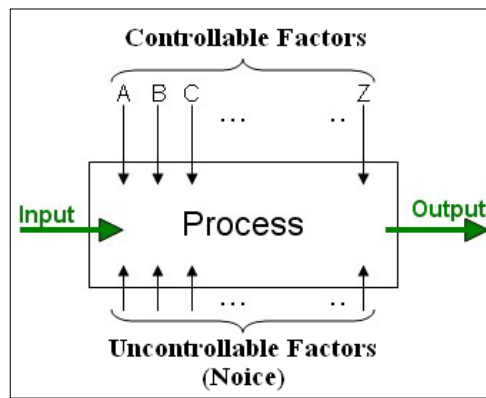
Figure 1.11: P-Diagram for Dynamic problems (Minitab 2001)

Further, to optimize the results obtained from these procedures and to make the analysis more precise, Response Surface Methodology (RSM) is incorporated (Sahoo et al. 2008). Response surface methodology (RSM) consists of a group of mathematical and statistical techniques used in the development of an adequate functional relationship between a response of interest, and a number of associated control (or input) variables. In general, such a relationship is unknown but can be approximated by a low-degree polynomial model (Andre and Siuli 2010).

1.8.4 Response Surface Methodology

In recent years, implementation of Response Surface Methodology (RSM) for addressing various problems has reported (Shang and Tadikamalla 2004). It is basically a sequential procedure for fitting a series of regression models to the output variables (Avila and Marcos 2003).

The basic objectives of this technique may be summarized as follows:

i.   Estimating a functional relationship between one or more responses and a number of independent variables that influence the responses.

ii.   Searching and exploring the optimum operating conditions for the system.

Conventionally, implementing the RSM methodology starts with a linear regression model as follows:

$$E(y) = a_0 + a_1x_1 + a_2x_2 + \cdots + a_kx_k \tag{1.11}$$

A low order polynomial (Eq. 1.12), called first order design, is generally selected to approximate the true function in some region of the independent variable (Shang et al., 2004). Thereafter, a higher order polynomial (Eq. 1.13), called second order design is employed to search for the general vicinity of the optimum region.

$$y = a_0 + \sum_{i=1}^{3} a_i x_i \cdot \tag{1.12}$$

$$y = a_0 + \sum_{i=1}^{3} a_i x_i + \sum_{i=1}^{3} a_{ii} x_i^2 + \sum_{i}\sum_{j \atop i<j} a_{ij} x_i x_j \tag{1.13}$$

In equations 1.11, 1.12 and 1.13 y is the desired response: a_0 is constant, a_i a_{ii} and a_{ij} represent the coefficients of linear, quadratic and cross-product terms, respectively, x_i represents the process parameter and i the number of levels (for eg. – three level experiment). Using this quadratic model for response function the objective is not only to investigate the response over entire factor space but also to locate the region where the response approaches its optimum or near optimal value. All the main parameters and their interactions are included for the initial analysis of the responses obtained from RSM. The model is then reduced by eliminating the terms with no significant effect on the response through the backward elimination process. The coefficient R^2 which is defined as the ratio of the explained variation to the total variation is a measure of the degree of fit for

the proposed model. When R^2 approaches unity, response model fits better with the actual data. In order to determine the optimal response point, the surface and contours are developed. From three dimensional surface plot and contour plot for the regression coefficient, revised operating parameters can be deduced.

Six Sigma methodology is a tool successfully used for optimization of the process (Koning and Mast 2004, Craig 2011, Tsao and Hocheng 2004). Adaptation of this technique to improve the quality of compression moulded gears of composites from recycled materials to achieve optimized low cost process and low cost recycled material is envisaged in this study. Such a combination of optimized low cost process and low cost recycled material could help producing low cost quality gears.

Polymers/polymer composites from recycled sources for bearing and gear applications are the subject of research owing to their resistance to corrosive environments. Most mechanical systems contain at least few gears. Computer printers have gears to feed paper and control printing heads; photocopiers and Automatic Teller Machines (ATMs) have literally dozens of such elements in each unit and gears are an integral part of many low tech products like toys and other gadgets (Kurakova et al. 2003). Some of the advantages of using polymer composite gears are low cost, less weight, high efficiency, quietness, and inertness to corrosive environment (Mao et al. 2010). These advantages make their successful use in the automotive industry, office machines, in food and textile machinery (Mao 2007) as well as for low tech products in toys and other gadgets (Kurakova et al. 2003). R-PET could be an alternative material for such low tech applications. Studies on the use of r-PET/r-HDPE composite for low tech gears have showed a positive prospect (Avila and Marcos 2003). However, a study on r-PET properties and process variables to develop it for moulding components at low cost is essential (Mao et al. 2010).

Thus the present study is focused on developing r-PET/FAC composite and optimizing compression moulding parameters for producing low cost components. However, to produce good quality components, material has to be developed and process parameters are to be tuned and optimized. Six Sigma based DMAIC/DMADV methodology is adapted. Objectives and scope of the present study are as follows.

1.9   OBJECTIVES AND SCOPE OF THE PRESENT WORK

It can be noted from the reviewed literatures that, r-PET based composites with FA cenospheres as reinforcement and compression moulding as a manufacturing process can lead to the requirements of an industry to produce low cost engineering components. However, to produce good quality components, both the process and the material parameters are to be optimized. In the process of optimization, Six Sigma based DMAIC/DMADV methodology along with Taguchi's method and RSM can be the useful tools. Based on these observations the present work is engaged with following objectives and the scope.

1.9.1 Objectives:

1. To identify the compression moulding process parameters for moulding r-PET using thermo-mechanical recycling and develop the process to achieve good samples.
2. To study the mechanical and wear properties of FAC reinforced r-PET (r-PET/FAC) composite samples made from the process developed above and understand the effect of material and process parameters.
3. Attempt to improve the properties of the composite by matrix blending and surface treatment of FAC.
4. To optimize compression moulding process parameters for the material developed above using Six Sigma approach and fabricate gears with the developed material and optimized process.
5. To test the gear life in order to establish the usefulness of this material in gears for low tech application.

1.9.2 Scope:

To develop the compression moulding process for r-PET using thermo-mechanical recycling to achieve good samples, Six Sigma DMADV methodology is adapted. Three moulding parameters at four levels are considered, Moulding time at 4, 6, 8 and 10 min, Moulding pressure at 2.5, 5, 7.5 and 10 MPa and Moulding temperature at 250, 260, 270 and 280˚C.

R-PET/FAC composite samples are moulded with four moulding variables viz. moulding temperature, pressure, time, cooling and one material parameter viz. FAC content. These variables are considered at three levels, Moulding temperature is considered at 50, 100 and 150˚C, moulding pressure at 5, 10 and 15 MPa, moulding time at 5, 10 and 15 min. the mould cooling variations are air cooling, water cooling and a combination of air cooling for 10 min. followed by water cooling. FAC is varied in the levels 5, 10 and 15% by weight. The mechanical (flexural) and wear properties of these samples are determined using DOE with five repetitions for each run. Results are analyzed statistically using MINITAB software.

R-PET is blended with five polymers viz. recycled linear low density polyethylene (r-LLDPE), recycled low density polyethylene (r-LDPE), recycled high density polyethylene (r-HDPE), recycled polypropylene (r-PP) and recycled Nylon (r-Nylon) independently in the proportion of 10 and 30% by weight for the preliminary study. Further, r-PET blended with 30% by weight of r-LDPE and reinforced with FAC at 5, 10 and 15% by weight are studied in detail. The effect of treating of FAC with 10% (3-Aminopropyl) trimethoxy silane (3APTMS) for better interface is also studied.

To optimize material and compression moulding process parameters for better composite samples, Six Sigma DMAIC approach with five parameters at three levels is considered. Two parameters, percentage of treatment with 3APTMS and percentage of r-LDPE constituents are considered. 3APTMS treatment is considered at 6, 8 and 10% by weight and r-LDPE at 10, 20 and 30% by weight. Again flexural and wear properties of the composite are used for optimization.

The blended r-PET reinforced with treated FAC (M-r-PET/T-FAC) composite gears are made with optimized process and tested at 250 rpm with step test method. The test is conducted with loads incremented by 5 N for every 15,000 rotations till the failure of the gear.

CHAPTER 2

MATERIALS AND METHODS

As outlined earlier, the objective of the present work is to develop compression moulding process for thermo-mechanical recycling of r-PET, and to develop and optimize r-PET/FAC composites using Six Sigma methodologies for moulding gears. Analysis on r-PET composite conducted during this work can be broadly classified in to five stages.

The first stage of the experimentation is carried out with an intention to establish a thermo-mechanical moulding process for r-PET. The r-PET bottles in the form of flakes, coarse powder and fine powder is used. Six Sigma DMADV methodology is utilized along with Failure Modes and Effects Analysis (FMEA) for successive improvement in the moulding procedure.

In the second stage, r-PET as matrix material reinforced with FAC is studied for a set of compression moulding process variables and material variables using design of experiments as statistical tool.

The third stage involves developing the composite with r-PET matrix blended with r-LDPE. Further, 3APTMS is used for the surface compatibilization of FAC and hence to improve the interface between r-PET matrix and FAC. The properties of all the materials used in the development of r-PET/FAC composite are described in this chapter.

In the fourth stage the developed process and material parameters of the composite are optimized for improved properties of the samples. Six Sigma DMAIC optimisation tool is used at this stage.

In the fifth and final stage the material developed in the previous stages is moulded into gears with optimized compression moulding and their performance is evaluated on a

indigenously designed and fabricated rig. The methodology adopted for development of moulding process and development of r-PET composite is pictured in the Figure 2.1.

Specifications and properties of the raw materials, process equipments used, design of experiments, procedures utilized for preparation of r-PET blends and composites and the testing methods adapted are described in this chapter. The details of the reagents/chemicals used at different stages of filler treatment are also described.
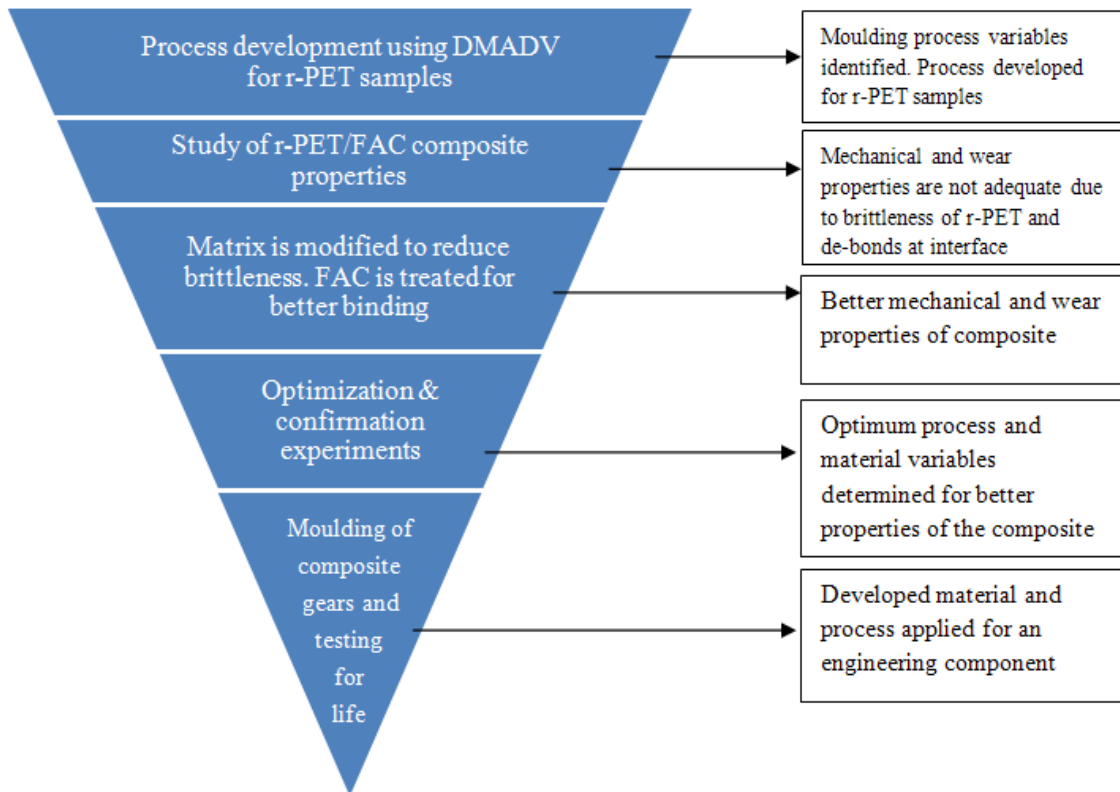
Figure 2.1: Methodology adopted for developing composite material and process.

2.1 MATERIALS
Different materials used in the work and their properties are discussed in this section

2.1.1 Matrix system
The matrix system used in this work is recycled Polyethylene terephthalate (r-PET). PET bottles of similar kind used as beverage packing bottles, retrieved by the recycling agencies are used. The properties of post r-PET are given in the Table 2.1(Seena et al. 2010).

Table 2.1: Properties of r-PET (Seena et al. 2010)

Molecular formula	$(C_{10}H_8O_4)$
Resin identification code	1
Density	1.4 g/cm^3 (20 ºC) (average)
Melting point	250°C to 260°C
Flexural modulus	1450 MPa
Flexural strength	20 MPa
Elongation at break	3%

2.1.2 Reinforcing filler

FAC is used as particle reinforcing agents for r-PET in this work. They are low density hollow constituents of FA having aspect ratios closer to unity and hence are expected to display near isotropic characteristics. These particles possess good mechanical properties and are also inexpensive. In the present study, FA from which FAC are separated is acquired from Raichur Thermal Power Plant Corporation Ltd., Raichur (India). This ASTM class 'C' fly ash (ASTM C 618) with bulk density of about 900 kg/m^3 and a true particle density of 2250 kg/m^3 (Narasimha Rao 1999) is found to consist a mixture of solid and hollow spheres of different sizes. The composition and physical properties of cenospheres is tabulated in the Table 2.2 (Navin and Pratibha 2008) and Table 2.3 (Ash Tech www.ashtechindia.com). The average density of FAC, thus obtained, is found to be 391 kg/m^3 and the average sizes is about 57 microns.

2.1.3 Recycled plastics for matrix blending

The material modifications performed in the third stage of the experimentation involves blending r-PET composite with r-LLDPE, r-LDPE, r-HDPE, r-PP and r-Nylon. All these plastics are acquired from M/s Janani plastics, Baikampadi, Mangalore (India). The properties of these polymers are mentioned below.

Recycled High-Density Polyethylene (r-HDPE)

The term polyethylene (PE) describes a huge family of resins obtained by polymerizing ethylene gas, $H_2C=CH_2$ and it is by far the largest volume of commercial polymer produced. The most famous commercial grades are low-density polyethylene (r-LDPE), medium-density (r-MDPE) and high-density polyethylene (r-HDPE). HDPE is defined by

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a density greater or equal to 0.941 g/cm^3. R-HDPE has a low degree of branching resulting in low intermolecular forces and low tensile strength. Although the density of r-HDPE is only marginally higher than that of low-density polyethylene, but due to its little branching, gives it stronger intermolecular forces and tensile strength than r-LDPE. The difference in strength exceeds the difference in density, giving r-HDPE higher specific strength. Cost of r-HDPE is Rs 40-50/Kg. The resin identification code for r-HDPE is 2.

Table 2.2: Compositional details of fly ash cenosphere particles

(Navin and Pratibha 2008)

Components	Wt %	Components	Wt %
SiO_2	56-60	Na_2O	0.5-2
Al_2O_3	25-35	K_2O	1-2
Fe_2O_3	1-6	MgO	0.5-2
CaO	0.2-0.6		

Table 2.3: Physical properties of fly ash cenospheres

(Ash Tech, www.ashtechindia.com)

Property	Value	Property	Value
Size of cenosphere	10-350 Microns	Compressive strength	20.7-34.5 MPa
pH in water	6.0-8.0	Softening point	980˚C
density	0.3-0.6 gm/cm^3	Shape	Spherical
Shell wall thickness	2-10 micron	Colour	Light Gray-Dark red

Recycled Low Density Polyethylene (r-LDPE)

The mass density range of LDPE is 0.910 to 0.940 g/cm^3. Made in translucent or opaque variations, it is quite flexible, and tough but breakable. r-LDPE has more branching (on about 2% of the carbon atoms) than r-HDPE, so its intermolecular forces (instantaneous-dipole induced-dipole attraction) are weaker, its tensile strength is lower, and its resilience is higher. Cost of recycled LDPE is in the range of Rs.35-40/Kg. The resin identification code for r-LDPE is 4.

Recycled Linear Low-Density Polyethylene (r-LLDPE)

R-LLDPE is defined by a density range of 0.915–0.925 g/cm^3. R-LLDPE is a substantially linear polymer (polyethylene) with significant numbers of short branches. R-LLDPE has higher tensile strength, higher impact and puncture resistance than r-LDPE. The chain formation is the only structural difference between r-LDPE and r-LLDPE. R-LLDPE has linear chain formation and has short branches. It is very flexible and elongates under stress. It can be used to make thinner films, with better environmental stress cracking resistance. It has good resistance to chemicals. The resin identification code for r-LLDPE is 4.

Recycled Polypropylene (r-PP)

Also known as polypropylene, it is a thermoplastic polymer used in wide variety of applications including packaging and labeling, textiles (e.g., ropes, thermal underwear and carpets), stationary, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers and automotive components. An additional polymer made from the monomer propylene is rugged and unusually resistant to many chemical solvents, bases and acids. Most commercial polypropylene is isotactic and has an intermediate level of crystallinity between that of r-LDPE and r-HDPE. The resin identification code for r-PP is 5.

Recycled Nylon (r-Nylon)

r-Nylon is a thermoplastic, silky material, first used commercially in a nylon-bristled toothbrush. R-Nylon is made of repeating units linked by amide bonds and is frequently referred to as polyamide. Nylon fibers are used in many applications including fabrics, bridal veils, carpets, musical strings, and rope. The resin identification code for r-Nylon is 7. The properties of the plastics considered in this study are tabulated in the Table 2.4.

2.1.4 Reagent used for the surface treatment of FAC

(3-Aminopropyl) trimethoxy silane (3APTMS) is the chemical used for coating the cenospheres for better interaction with the matrix (Seena Joseph et al. 2010). Silane coating is an adsorption process in which Silane is coated on the surface of cenospheres. Here the focus is on the main constituent radical amine group NH$_2$. The radical amine group will help in bonding cenospheres and matrix material (PET), which enhances the

mechanical properties of the composite. Chemical structure of silane coupling agent (3-Aminopropyl) trimethoxy silane, is as shown in the figure below. In the figure, we can see NH_2 group which will help in binding the cenospheres with r-PET/r-LDPE blend. The chemical structure of 3APTM Silane is shown in the Figure 2.2.

Table 2.4: Properties of plastics used for blending with r-PET

Sl. No.	Properties	Unit	Plastics				
			HDPE	LLDPE	LDPE	PP	NYLON
1	Young's Modulus	MPa	600-1400	250-700	200-400	1100-1550	2000-4000
2	Elongation	%	180-1000	500-900	600-650	200-700	-
3	Bending Strength	MPa	20-45	-	10-40	30-42	-
4	Yield strength	MPa	-	20-30	15-20	-	23-27
5	Melting Temperature	$^\circ$C	210-234	222-247	220-246	211-225	230-260
6	Density	g/cm^3	0.94-0.96	0.911-0.943	0.910-0.928	0.902-0.906	1.15-1.46
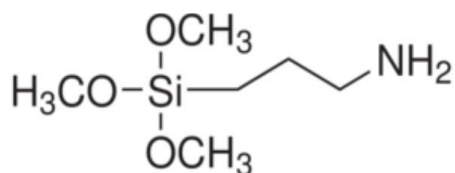
Figure 2.2: Chemical structure of silane coupling agent (3-Aminopropyl)trimethoxysilane

Table 2.5: Properties of 3APTM Silane coupling agent

Properties	Values
Physical state	Liquid
Density	1.025 g/cm^3 at 25^{0}C
Boiling Point	91^{0}C-92^{0}C

2.2 METHODS

Methods used in preparing the raw materials, procedure for moulding composites, experimental designs adapted and sample testing methods are described in the following sections.

2.2.1 Preparation of r-PET for recycling

The PET bottles of similar kind used in beverage packing industries, retrieved by the recycling agencies are used. The caps and the labels attached on the bottles are separated and the bottles are cut into quarter in size. The plastic thus obtained is initially washed with dilute solution of detergent to remove dirt, glue and other impurities and finally with clean water. The clean plastic thus obtained is extensively dried and cut into smaller flakes using an industrial granulator and grinded to powder form using a grinder. Ground powder is essential in the first stage of experimentation which was conducted to establish and optimize a moulding technique for mechanical recycling of r-PET. However, from the second stage onwards the experiments are conducted using granulated r-PET. Figures 2.3 A and 2.3 B display r-PET in flake and powder forms respectively.
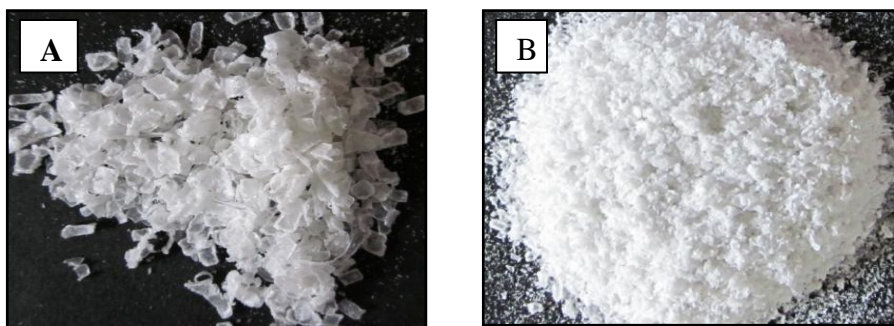
Figure 2.3: Flakes (A) and the Powder (B) of r-PET used for moulding

2.2.2 Extraction of FAC from FA

FAC are constituents of FA which is a by product of thermal power plants. The density of FAC is much lower than FA, hence density separation method is adapted to extract FAC from FA. The FA is thoroughly mixed to form dilute slurry in a large container. The slurry is allowed to settle down for about 24 hrs and FAC float to the surface. The FAC are filtered using a filter paper. The FAC collected in the paper are dried and the ferrous impurities are separated magnetically. The mass is burned to burnout organic impurities

and moisture and FAC are stored in an oven. FAC separation setup and the FAC thus collected are shown in the Figures 2.4 and 2.5 respectively. Some of the parameters used for obtaining FAC from FA are tabulated in the Table 2.6
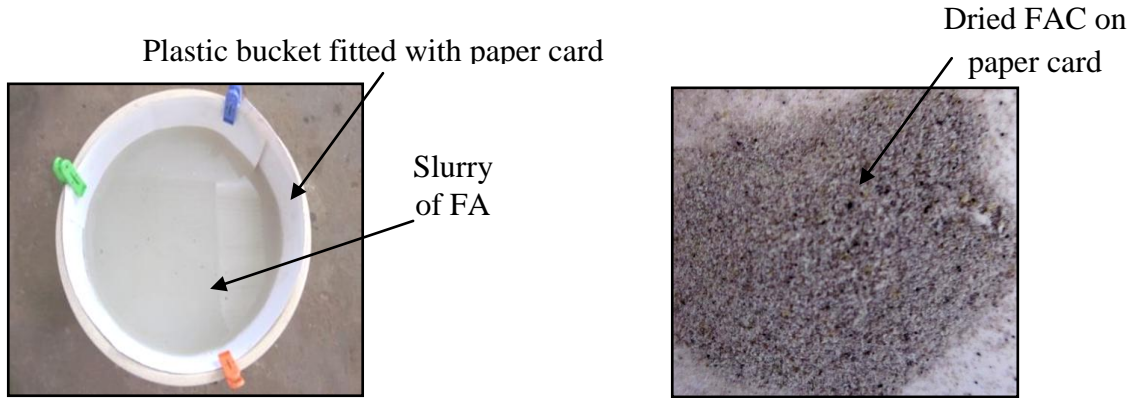
Figure 2.4: Slurry and floating FAC

Figure 2.5: Dried FAC

Table 2.6: Parameters used to extract cenospheres from Fly ash

Sr. No.	Parameter	Metric
1	Weight of fly ash	1 Kg
2	Quantity of Water	13 Litres
3	Capacity of bucket	15 Litres
4	Settling time for fly ash	24 hrs
5	Sieve	300 Microns
6	Drying temperature	150 ^{0}C
7	Drying time	2 hrs

2.2.3 Compression moulding method

A programmable compression moulding machine supplied by PLUS ONE MACHINEFABRIK (Belgaum, India), shown in the Figure 2.6 is used for moulding samples for flexural as well as wear tests. The specifications of the moulding machine are tabulated in Table 2.7. The r-PET granules along with other constituents in required proportion by weight are premixed and converted into a mushy charge by heating it

around the processing temperature. The material is then charged in to the cavity of the hot mould. The mould is closed with plunger halve and the r-PET charge is moulded at a set pressure. After pre decided testing time, the mould is unloaded from the machine and after cooling the sample is ejected from the mould. Apart from the constituents of the composite, moulding pressure, temperature and time are the process variables used at multiple levels as discussed in detail in the subsequent section.

Figure 2.6: Compression moulding machine

Table 2.7: Specifications of compression moulding machine

Description	Specification
Manufacturer	PLUS ONE MACHINEFABRIK (Belgaum, India)
Capacity	32 tones
Ram stroke	200 mm
Day light	200 mm
Platen size	250×250 mm
Pressure	51.2 kg/Cm^2 Specific
Heating capacity	1.5 kW/platen

2.2.4 Moulds for compression moulding

The three common types of mould used in compression moulding are explained in section 1.6.2. Proper designing of the mould is an important aspect for producing good quality products. Among the three types of compression moulds, open flash type of mould is useful for experimental purpose, hence it is considered in our study. The dimension of flexural samples is 80×40×4mm in accordance with ASTM D790 standard. The design details of the mould are displayed in the drawing Figures 2.7 and 2.8.
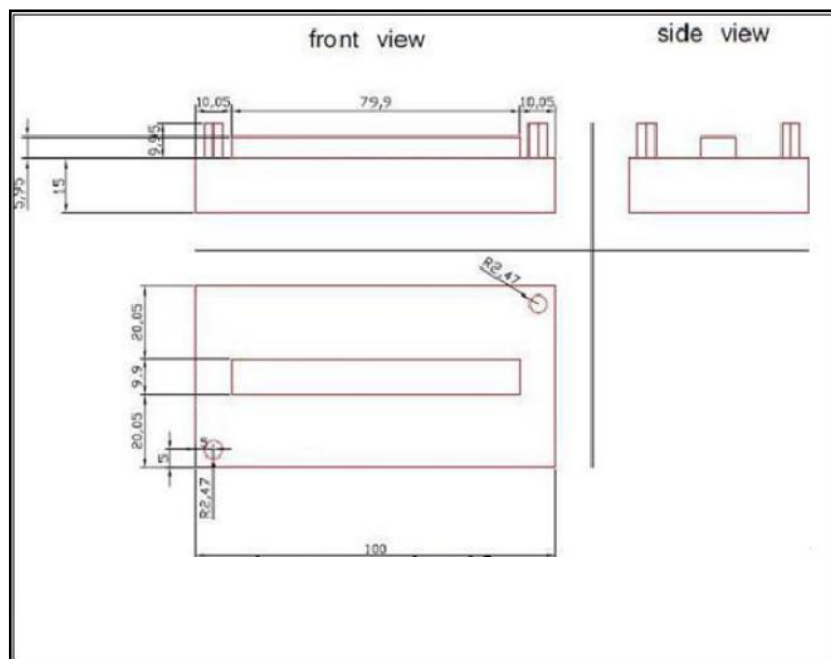
Figure 2.7: Insert halve or plunger mould halve

The clearance between the plunger and the cavity halves is maintained in the range of 0.025 - 0.050 mm on each side. Ejector pins and air vents as per the requirements are provided for easy ejection of the samples from the mould and for the escape of entrapped gasses. The air vents of dimension 20×2×0.5 mm for long side and 10mm×2mm×0.05 mm for shorter side of the mould is provided. The picture of the mould is in Figure 2.9.

A gear from electronic printer is chosen as a target application. The test gear is of 36 teeth with 1.197 module. A compression mould with this specification is designed and fabricated. Figure 2.10 exhibit the mould utilised for manufacturing the polymer gears.
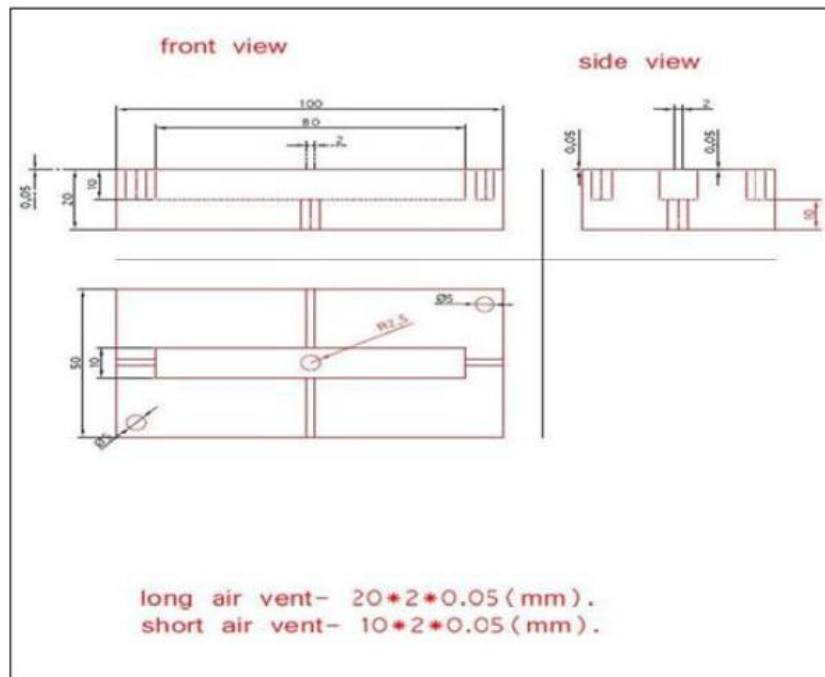
Figure 2.8: Cavity Halve of the mould

Figure 2.9: Open flash type compression mould for flexural and wear samples

2.2.5 Sample preparation for flexural tests

The mass of different constituents required to mould the composite is calculated on the weight percent method. Prior to moulding, the mould is prepared to minimise sticking of the polymer onto the surface. A Teflon adhesive is attached to the bottom face and the sides of the mould are covered with silicone releasing compound (Metroark-211[®]). With

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the releasing agent in place, the mould is heated to the moulding temperature in the range of 50 - 150°C in the compression moulding machine. The constituents of the composite are weighed and mixed thoroughly in a container and on an electric heater (Figure 2.11).

Figure 2.10: Mould for compressing gear samples.

The charge is continuously stirred during heating to facilitate uniform distribution of the constituents of the composite. The mass is allowed to turn into a mushy charge. The hot mould is then opened and filled with the charge. The plunger half of the mould is closed and moulding pressure for pre decided time is applied (Figure 2.12). On completion of moulding, the mould is unloaded from the machine and cooled either under water or in air or a combination of both. Finally, the sample is ejected from the mould and cleaned by removing flash formed during moulding. The final sample is shown in the Figure 2.13. Every sample with varying contents of FAC, r-LDPE and 3APTMS are moulded with the procedure specified as above.

2.2.6 Sample preparation for wear studies

The r-PET composite samples are prepared for testing their wear properties in accordance with ASTM G 99-95 standards. The samples for wear test with a dimension 8mm×8mm×4mm (64 mm^2 contact area) are cut from the compression moulded flexural specimen (80mm×10mm×4mm) to accommodate in a press fit sample holder of same

dimension. A sample ready to use for testing and a mounted sample in the holder are shown in the Figure 2.14.

Figure 2.11 Electric heater used for the preparation of the charge.

Figure 2.12 Mould maintained under pressure.
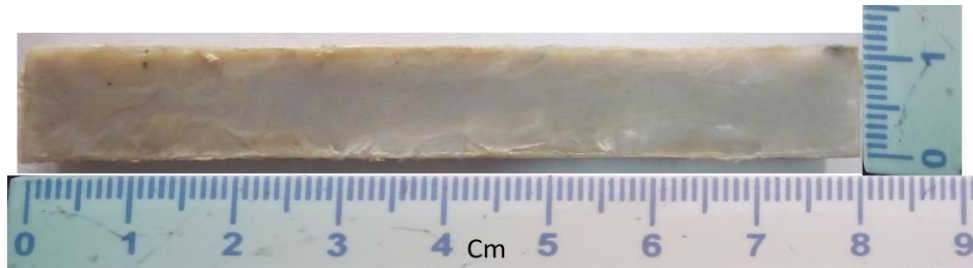
Figure 2.13: Moulded sample for flexural test.
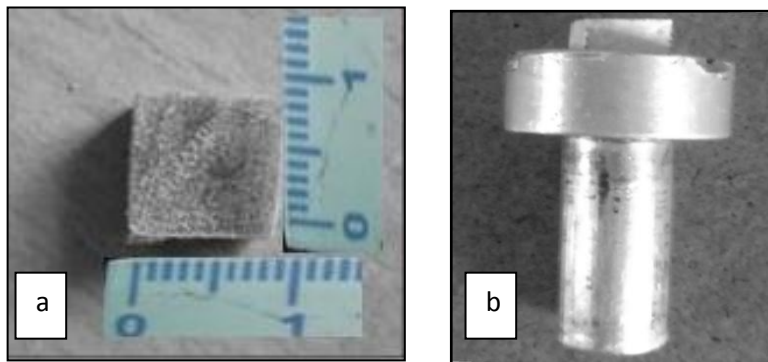
Figure 2.14: Sample for the wear tests (a), mounted on a fixture (b)

2.2.7 Surface treatment of cenospheres

The cenospheres are treated with (3-Aminipropyl) trimethoxy silane (3APTMS). Initially, FAC is cleaned with acetone and dried at 60^0C in hot air circulating oven for around one hour. Isopropyl alcohol is the solvent used. The 3APTM silane is mixed at different percentage by volume of isopropyl alcohol in the beaker along with FAC. Continuous

stirring is carried out by magnetic stirrer for around 4-5 hours and then the mixture is kept in hot circulating oven at $65 - 70\,^0$C for about 14 to 16 hours. The mixture is heated until all the solvent evaporates leaving behind the silane coated FAC. The coated filler is preserved in a desiccator to prevent any attack of moisture and atmospheric oxygen.

2.3 EXPERIMENTAL DESIGNS

Different procedures followed to conduct various experiments on r-PET composites are dealt in this section. Six Sigma DMADV tool is used for developing the moulding process for r-PET in the first stage. Taguchi's design of experiments is adapted in the second and the fourth stage to evaluate flexural and wear properties of r-PET composites. This section also includes the experimental plan for processing and experimenting r-PET/FAC composite for mechanical and wears properties.

2.3.1 Six Sigma DMADV methodology for moulding r-PET

Compression moulding process is developed for moulding r-PET using Six Sigma DMADV methodology. This methodology is generally used for optimizing a new process. In the present study, DMADV is incorporated to develop the process for moulding r-PET using compression moulding process. The following section deals in the techniques of Six Sigma DMADV methodology.

Define

The objective of performing this exercise is to optimize compression moulding process for r-PET.

Measure

After critical analysis of parameters influencing compression moulding process, the significant ones, critical to quality (CTQ) considered for the study are moulding temperature, molding pressure and moulding time. A discussion of these CTQs' follows below

- *Moulding temperature:* Compression moulding is essentially a process that involves applying temperature and pressure. An increase in the temperature at which the plastic is moulded, reduces the viscosity and improve the flow of plastic. At a

temperature above Glass transition temperature (T_g), the modulus drops drastically and is low enough to achieve flow and shape for the plastic. Overheating, however, degrades the plastic.

- *Moulding pressure:* The softened hot polymer can flow to every possible space of the mould on applying external pressure to yield the required shape. On applying insufficient pressure, the movement of the plastic is inadequate to yield a near net shape. Excessive pressure, on the other hand, results in reduction in size, formation of excessive flash and material wastage.

- *Moulding time:* Flow of polymer in the mould to take the shape of the product is essential in thermoplastics. The time taken by the plastic to obtain the shape of mould cavity is moulding time. Insufficient time leads to incomplete moulding and excessive time cause disintegration or char formation.

Figure 2.15 shows the Cause effect diagram visually representing the dependence of quality on process parameters.
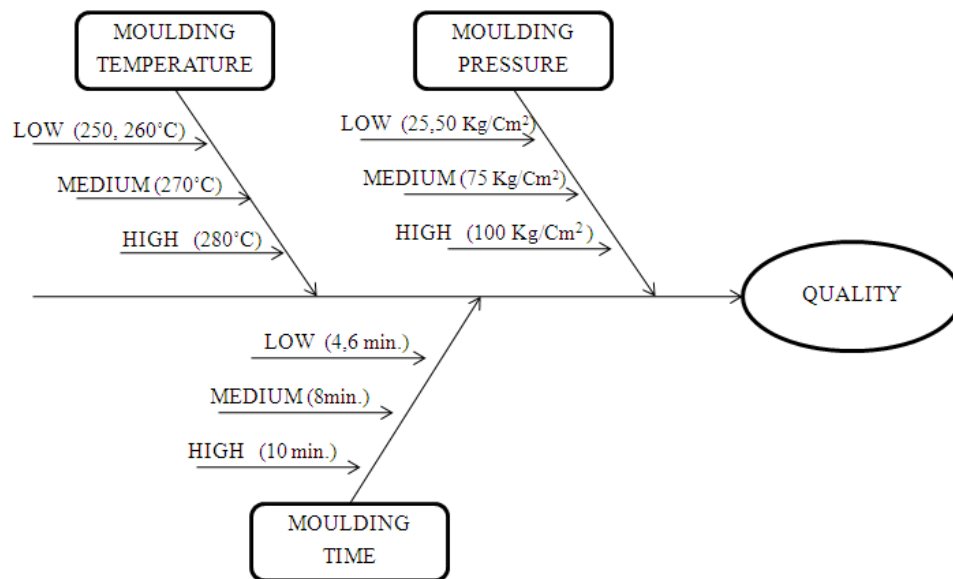
Figure 2.15: Cause - effect diagram for moulding r-PET

Further, moulding r-PET by charging the mould with flakes leads to the formation of large voids in the sample as displayed in the Figure 2.16. Further, the samples are found to be very brittle and easily breakable due to presence significant amounts of voids in the matrix.
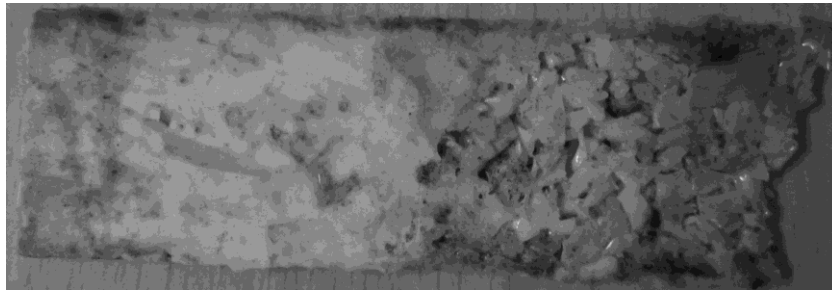
Figure 2.16: Large voids in the moulded r-PETsample

Analyze

The void formation in the r-PET samples is analysed to be due to entrapment of air molecules between flakes in the mold. In order to improve the moulding process for reducing voids in the samples, Taguchi's method of experimental design with L_{16} orthogonal array is utilized.

Design

In this section, the process for moulding r-PET through compression moulding route is designed. The design verification and optimisation of the process is achieved by sequentially examining the outcome of pilot runs followed by redesign. The method adapted to mould fairly good samples and the experimental plans are described in this section.

Three parameters viz. factor A: moulding time, factor B: moulding pressure and factor C: moulding temperature are considered at four levels. Table 2.8, depicts the various parameters with their corresponding levels. The levels of each of the parameters were decided from prior experiences and the existing conditions. The L_{16} orthogonal array is constructed with moulding time, temperature and pressure as controlling parameters. Minitab release 14 software was used to construct the orthogonal array. This array assigns 16 runs and the array thus constructed is shown in the Table 2.9.

The results of testing the samples for properties are explained in the Chapter 3 (Section 3.1). Failure Modes and Effects Analysis (FMEA) methodology is adopted to improve the moulding process leading to reduction in the defects.

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Table 2.8 CTQ process parameters and their levels for moulding r-PET

Factor	Process parameter	Range	Level -1	Level -2	Level -3	Level -4
A	Moulding time (Min)	4-10	4	6	8	10
B	Moulding pressure (MPa)	2.5-10	2.5	5.0	7.5	10
C	Moulding temperature (˚C)	250-280	250	260	270	280

Table 2.9: L_{16} Orthogonal Array utilized for moulding r-PET

Expt. No.	Moulding Time (Min)	Moulding Press(kg/cm^2)	Moulding Temp. (˚C)
1	4	25	250
2	4	50	260
3	4	75	270
4	4	100	280
5	6	25	260
6	6	50	250
7	6	75	280
8	6	100	270
9	8	25	270
10	8	50	280
11	8	75	250
12	8	100	260
13	10	25	280
14	10	50	270
15	10	75	260
16	10	100	250

2.3.2 Failure modes and effects analysis

Failure modes and Effects Analysis is a well established quality management method used for the analysis of potential failure modes within a system for classification by the severity and likelihood of the failures. This method relies on rating the quality of the samples based on Severity (S), which defines the severity of the effects of the failure mode and occurrence (O), that looks into the cause of a failure mode and number of times it occurs and detection (D), a measure of the risk that the failure will escape detection. These parameters are rated on a reference given in Tables 2.10 and 2.11 respectively. Further, these parameters are tabulated in a FMEA work sheet, a sample of which is provided in Table 2.12.

The Risk Priority Number (RPN=S×O×D) (Otto et al. 2001) helps in determining the areas of greatest concern for failure. It helps in choosing an appropriate action against failure modes.

Table 2.10: Rating table for severity and occurrence

Rating	Meaning
1	No effect
2/3	Low (relatively few failures)
4/5/6	Moderate (occasional failures)
7/8	High (repeated failures)
9/10	Very high (failure is almost inevitable)

Table 2.11: Reference Table for detection rating

Rating	Meaning
1	Almost certain
2/3	High
4/5/6	Moderate
7/8	Low
9/10	Very remote to absolute uncertainty

Table 2.12: Sample FMEA Worksheet to evaluate the process outcome

Func-tion	Failure Mode	Effects	Severity Rating (S)	Causes	Occurr-ence Rating (O)	Current Controls	Detection Rating (D)	Risk Priority Number (RPN)	Recomm-ended Action	Action Taken
								S×O×D		

2.3.3 Taguchi's DOE for moulding R-PET/FAC composites (flexural properties)

In this stage of experimentation, the objective is to understand the effect of FAC on the properties of r-PET. Figure 2.17 shows the cause and effect diagram drawn from the process parameters. Steps involved in applying Taguchi's method of design of experiments, which are explained in the section 1.8.3, are elaborated below.

The five CTQs viz. factor A, moulding pressure; factor B, moulding time; factor C, mould cooling; factor D, moulding temperature and factor E, weight fraction of cenospheres, are analyzed at three levels as nonlinear behaviour of the parameters can be determined if more than two levels are used (Syrcos 2003). Table 2.13, depicts these parameters/factors with their corresponding levels. The levels of each of the parameters are decided from prior experience. Owing to high probability, effect of interactions between various process parameters on the flexural properties, the interactions of these parameters is also studied. As depicted in the linear graph (Figure 2.18), the interactions between the moulding temperature and mould cooling (C×D), moulding temperature and weight fraction (C×E) and the moulding temperature and weight fraction (D×E) are tested. The total number of degrees of freedom (DOF) for five factors at three levels and three interactions are found to be '22'. Therefore, a three level orthogonal array with at least '22' DOF is selected.
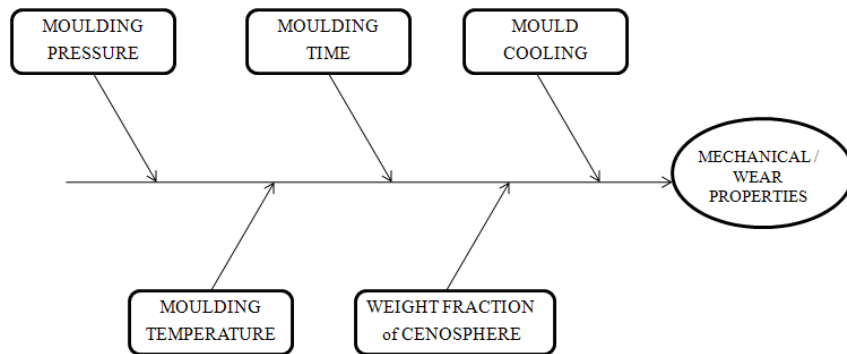
Figure 2.17: Cause and Effect diagram for analyzing r-PET/FAC composite.

Table 2.13: CTQ parameters and levels of them adopted for studying

r-PET/FAC composites

Factor	Process parameter	Range	Level 1	Level 2	Level 3
A	Moulding pressure (MPa)	5-15	5	10	15
B	Moulding time (Min)	5-15	5	10	15
C	Mould Cooling type	1-3	Water(1)	Air (2)	1 + 2
D	Moulding temperature (˚C)	50-150	50	100	150
E	Weight fraction of FA Cenospheres (%)	5-15	5	10	15

From the Taguchi's orthogonal inner arrays, the L_{27} (3^{13}) design for controllable factors as shown in Table 2.14, is selected. Minitab release 14 software is used to construct and analyse the orthogonal array. This array assigns 27 experimental runs and has 13 columns. The linear graph for the L_{27} (3^{13}) orthogonal array is shown in Figure 2.18. Each circle in the linear graph represents a column within the orthogonal array. The line joining the circles represents the interaction between the two factors displayed by circles. The number accompanying the line segment represents the column within the array to which the interaction should be assigned.
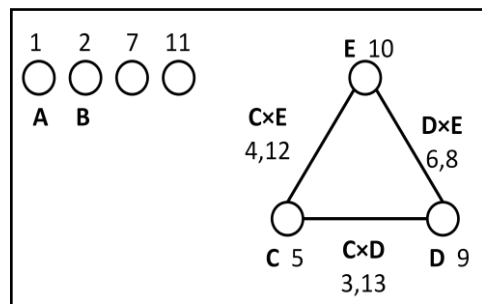
Figure 2.18: Linear graph for assigning CTQs and their interactions to OA.

According to the linear graph, columns 1, 2, 5 in L_{27} (3^{13}) are assigned to factors A–C, and factors D and E are assigned to columns 9 and 10. Columns 3 and 13 are reserved for the interaction between C and D. Similarly, columns 4 and 12 are assigned for the interaction between C and E and column 8 for that between D and E. The interaction between C, D and E is assigned in the column 6 as illustrated in Table 2.14. Other

columns (7 and 11) are left unassigned. A similar design can be found in the work by Syrcos (2003).

Table 2.14: Orthogonal array L_{27} (3^{13}) taken into consideration for testing flexural properties of r-PET/FAC composite

Trial	A	B	C×D	C×E	C	C×D×E		D×E	D	E		C×E²	C×D²
	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2	2	2	2
3	1	1	1	1	3	3	3	3	3	3	3	3	3
4	1	2	2	2	1	1	1	2	2	2	3	3	3
5	1	2	2	2	2	2	2	3	3	3	1	1	1
6	1	2	2	2	3	3	3	1	1	1	2	2	2
7	1	3	3	3	1	1	1	3	3	3	2	2	2
8	1	3	3	3	2	2	2	1	1	1	3	3	3
9	1	3	3	3	3	3	3	2	2	2	1	1	1
10	2	1	2	3	1	2	3	1	2	3	1	2	3
11	2	1	2	3	2	3	1	2	3	1	2	3	1
12	2	1	2	3	3	1	2	3	1	2	3	1	2
13	2	2	3	1	1	2	3	2	3	1	3	1	2
14	2	2	3	1	2	3	1	3	1	2	1	2	3
15	2	2	3	1	3	1	2	1	2	3	2	3	1
16	2	3	1	2	1	2	3	3	1	2	2	3	1
17	2	3	1	2	2	3	1	1	2	3	3	1	2
18	2	3	1	2	3	1	2	2	3	1	1	2	3
19	3	1	3	2	1	3	2	1	3	2	1	3	2
20	3	1	3	2	2	1	3	2	1	3	2	1	3
21	3	1	3	2	3	2	1	3	2	1	3	2	1
22	3	2	1	3	1	3	2	2	1	3	3	2	1
23	3	2	1	3	2	1	3	3	2	1	1	3	2
24	3	2	1	3	3	2	1	1	3	2	2	1	3
25	3	3	2	1	1	3	2	3	2	1	2	1	3
26	3	3	2	1	2	1	3	1	3	2	3	2	1
27	3	3	2	1	3	2	1	2	1	3	1	3	2

2.3.4 Experimentation for wear studies of r-PET composites (Taguchi method)

Nine parameters at three levels are studied for wear properties of r-PET composites. Four moulding parameters, one material property and four wear properties sum to these nine parameters (Table 2.15). Full factorial experiments conducted for nine operating parameters, studied at three levels with five samples each for a combination of experiments lead to over nineteen thousand samples to study. On the other hand, Taguchi's DOE method provides similar results on studying one hundred thirty five samples. Lower cost and less time for experimentation is the reason behind selecting Taguchi's route of experiments. Table 2.15, depicts the various parameters with their corresponding levels.

Table 2.15: CTQ process parameters and their levels for the wear studies of r-PET/FAC composite

Factor	Process parameter	Range	Level 1	Level 2	Level 3	Column No.
A	Moulding pressure (M Pa)	5-15	5	10	15	1
B	Moulding time (min)	5-15	5	10	15	2
C	Load on specimen (kg)	1-3	1	2	3	3
D	Sliding distance (meter)	150-450	150	300	450	4
E	Mould Cooling type	1-3	Water(1)	Air (2)	1 + 2	5
F	Speed of rotation (rpm)	200-600	200	400	600	6
G	Roughness of surface (grade of SiC abrasive paper)	220-600	220	400	600	8
H	Moulding temperature (˚C)	50-150	50	100	150	9
I	FA Cenosphere (%)	5-15	5	10	15	10

The total number of degrees of freedom (DOF) for nine factors at three levels is found to be '18'. Therefore, a three level orthogonal array with at least '18' DOF is selected. From the Taguchi's orthogonal inner arrays, the L_{27} (3^{13}) design for controllable factors is selected. This array assigns 27 experimental runs and has 13 columns. The L_{27} orthogonal array is constructed by assigning nine columns to the control parameters which lead to

four unassigned columns. The OA considered for sample preparation is the same as one tabulated in Table 2.14 except the assignment of columns which is presented in the last column of the Table 2.15. Parameter A is assigned to the first column of the OA, parameter B to the second column and so on.

2.3.5 Preliminary experiments for matrix modifications of r-PET

The basic objective of conducting the experiments of the 3rd stage is to understand the effects of matrix and filler modifications on the properties of r-PET composite. The third stage of experimentation can be considered in two levels. In the first level, matrix is modified with an intention to improve its flexibility. R-PET is blended independently with r-LLDPE, r-LDPE, r-HDPE, r-PP and r-Nylon and tested for the mechanical and wear properties. These five recycled plastics are blended with r-PET in 10 and 30% proportion.

2.3.6 Experiments for investigating effect of blending the matrix and FAC treatment

In this stage, r-PET is blended with r-LDPE at 30% by weight and reinforced with 5, 10 and 15% by weight of FAC. The composites, represented as M-r-PET/FAC, are tested for flexural and wear properties. In the next stage r-PET is reinforced with treated FAC (T-FAC) at 10% of 3APTMS. T-FAC is varied in 5, 10 and 15% by weight. These composites, named as r-PET/T-FAC. The last stage of material modifications is devoted to study the effect of matrix blending and FAC treatment on the properties of the composite (M-r-PET/T-FAC). The matrix is blended with 30% by weight of r-LDPE and FAC are treated with 10% by weight of 3APTMS. All of these composites are tested for flexural and wear properties.

2.3.7 Design of experiments for M-r-PET/T-FAC composites (flexural properties)

The modified r-PET composite differs from the unmodified composite in such a way that the matrix is blended with r-LDPE and the FAC are surface treated with 3APTM Silane. The control parameters viz. moulding time and mould cooling type studied in the unmodified composite are replaced by r-LDPE and 3APTMS content in the composite. The other parameters considered are moulding pressure, temperature and FAC content.

The CTQ parameters and their levels considered in the present study are tabulated in Table 2.16.

Five parameters (A-E) considered at three levels lead to 22 numbers of degrees of freedom. A L_{27} orthogonal array as in Table 2.14 is considered. The assignment of main parameters to the columns of OA is provided in the last column of Table 2.16.

Table 2.16: CTQ parameters and their levels adopted for evaluating mechanical properties of M-r-PET/T-FAC composite

Factor	Process parameter	Range	Level 1	Level 2	Level 3	Column No.
A	Moulding pressure (M Pa)	5-15	5	10	15	1
B	3APTM Silane (%)	6-10	6	8	10	2
C	r-LDPE (%)	10-30	10	20	30	5
D	Moulding temperature (˚C)	50-150	50	100	150	9
E	FA Cenosphere (%)	5-15	5	10	15	10

2.3.8 Design of experiments for wear properties of M-r-PET/T-FAC composites

The experimental plan to study wear properties of M-r-PET/T-FAC composite is similar to that adopted for r-PET/FAC composite (Tables 2.14, 2.15) with an exception that moulding time and mould cooling type are replaced by % of treatment and % of r-LDPE in the columns 2 and 5 respectively. The levels for 3APTMS are 6, 8 and 10% by weight and that for r-LDPE are 10, 20 and 30% by weight. The CTQ parameters considered for the wear study, their levels and column assigned in L_{27} OA are displayed in the Table 2.17.

Table 2.17: CTQ parameters, their levels and column number assigned for studying wear properties of M-r-PET/T-FAC composite

Factor	Process parameter	Range	Level 1	Level 2	Level 3	Column No.
A	Moulding pressure (M Pa)	5-15	5	10	15	1
B	3APTMS (%)	6-10	6	8	10	2
C	Load on specimen (kg)	1-3	1	2	3	4

D	Sliding distance (meter)	150-450	150	300	450	4
E	r-LDPE (%)	10-30	10	20	30	5
F	Speed of rotation (rpm)	200-600	200	400	600	6
G	Roughness of surface (grade of SiC abrasive paper)	220-600	220	400	600	8
H	Moulding temperature (˚C)	50-150	50	100	150	9
I	Weight fraction of FAC (%)	5-15	5	10	15	10

2.4 FLEXURAL AND WEAR TESTING METHODS

The samples of r-PET composite manufactured through compression moulding route, are tested for their flexural and wear properties. These testing methods are explained in this section.

2.4.1 Testing of r-PET composite samples for flexural properties

The flexural test measures the force required to bend a beam under three point loading conditions. The bending samples of dimension $80 \times 14 \times 4$ mm, prepared in accordance with ASTM D790 standards, on the Compression Moulding machine is tested for flexural properties. A high-performance ZWICK/ROELL Z020 universal testing machine supplied by Zwick GmbH & Co. KG Germany is used for testing. The flexural test which is also called as three point bend test involves supporting the sample on two support rollers near the ends of the sample. The load is applied at the center of the specimen with a cross head at a specified speed prescribed by the standard. The UTM and the specimen mounting are shown in the Figure 2.19.

The important parameters to be considered for the tests are the support span, the speed of the loading, and the maximum deflection for the test. These parameters are based on the test specimen thickness and are defined by ASTM D790. As per the standards the test is stopped when the specimen reaches 5% deflection or the specimen breaks before 5%. The test parameters and corresponding metric is tabulated in the Table 2.18.
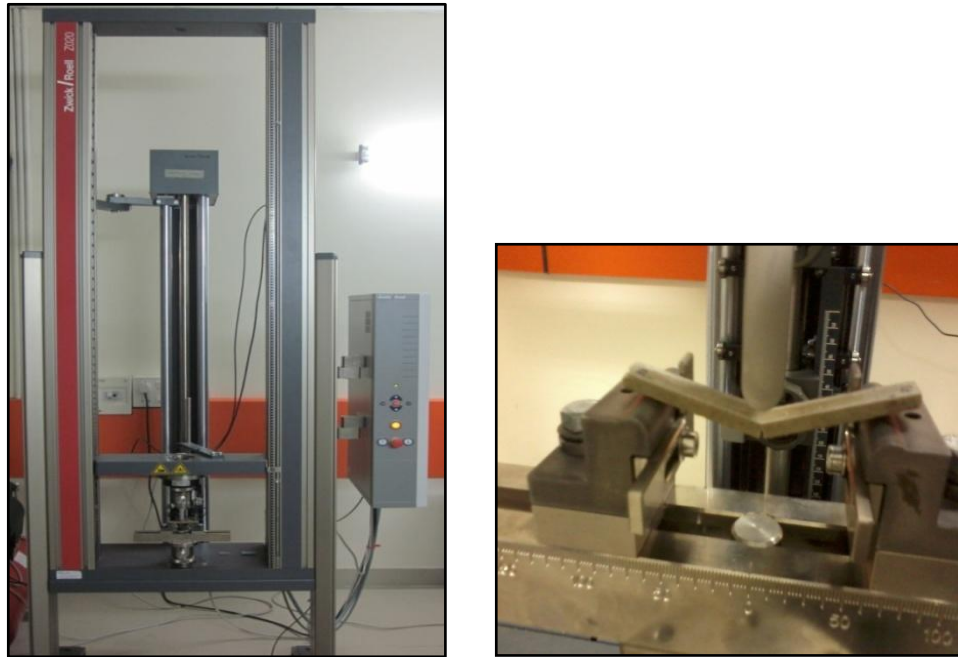
Figure 2.19: Universal Testing Machine used for flexural tests.

Table 2.18: Parametric settings for Universal Testing Machine

Sr. No.	Parameters	Metric
1	Standard used	ASTM D790
2	Sample size	80mm×10mm×4mm
3	Support span	50mm
4	Crosshead speed	2mm/min
5	Crosshead radius	5mm
6	Support roller radius	5mm
7	Maximum deflection	5%

2.4.2 Sample testing for wear properties

The r-PET composite is tested for wear properties in accordance with ASTM G 99-95 standards. The samples are tested on a wear and friction monitor TR-201CL (pin-on-disc). This is a Linear Variable Differential Transformer (LVDT) based sturdy versatile machine which facilitates study of friction and wear characteristics in sliding contacts under desired conditions. Sliding occurs between the stationary pin and the rotating disc.

Normal load, rotational speed and wear track diameter can be varied to suit the test condition. Tangential frictional force in Newton and wear in micrometers can be monitored with electronic sensors. A pin on disc setup is schematically represented in the Figure 2.20. The specifications of TR-201CL pin-on-disc machine is tabulated in the Table 2.19.
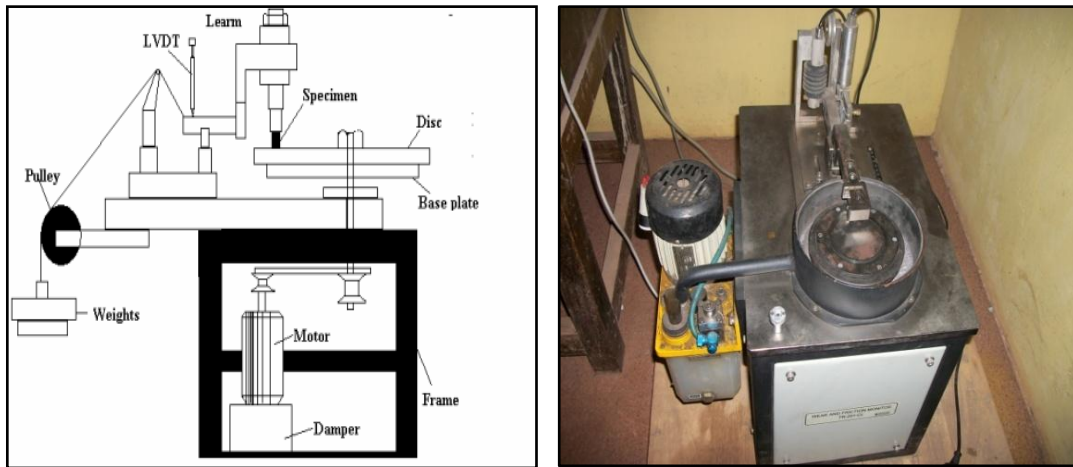
Figure 2.20: Schematic diagram of pin-on-disc setup and TR-201CL.

Table 2.19: Specifications of TR-201CL Pin on Disc machine

Parameters	Unit	Minimum	Maximum
Wear disc diameter	mm	---	100
Thickness	mm	6	8
Pin diameter	mm	3	10
Length	mm	10	30
Wear track diameter	mm	10	80
Disc speed	RPM	0	800
Normal load	N	0	100
Frictional force	N	0	100
Wear range	Mm	0	2
Power	V/Ph/Hz	230/1/50	

The test samples cut to the standard dimensions are rubbed over a 600 grade SiC paper to ensure proper contact with the counter surface. Their initial weight is recorded using a high precision Precisa XB120A electronic balance (0.1 mg accuracy) after thorough cleaning with soft paper soaked in acetone. The counter face disc is covered with a 400 grit SiC paper and the paper is changed for every test specimen in order to ensure constant roughness to which all the specimens are exposed. The sample is loaded with a dead weight through a string to which a pan assembly is attached. The wear parameters used for testing r-PET composites during material development stages that uses simple experiments are tabulated in the Table 2.20. However, the Taguchi experiments are conducted with the parametric settings as specified by the corresponding OA. After fixing both the disc and the sample (30mm track diameter) in their respective positions, the normal load to the sample is applied through a pivoted loading lever with a string as shown in Figure 2.20. Once the sample is tested for the required sliding distance, the test is stopped using a timer mechanism provided in the machine and the final weight of the sample is measured. A minimum of five tests are carried out for each composition of the material and the weight loss is recorded.

In order to verify the coating of silane on FAC, Fourier transformation infra red spectroscopy (FTIR) and Thermo gravimetric analysis (TGA) are conducted. The FTIR spectrometer and TGA equipment used in this study are shown in the Figure 2.21. Prior to the testing of the sample, FTIR is calibrated for air to nullify the errors. The sample to be tested is then taken in powdered form and is kept below the probe. The absorption spectrograph is explained in Chapter 3.

2.4.3   Experiments for investigating the performance of M-r-PET/T-FAC gears

The gear test rig shown in Figure 2.22 is indigenously designed and developed for testing r-PET/FAC composite gears. It houses a 3 hp electric motor with 4 speed gear box. The test gear is of 36 teeth with 1.197 module. The driving gear is made of Cast iron having same module and 72 numbers of teeth. Brake drum diameter is 115 mm. The gears are tested at a fixed speed of 250 rpm. Accelerated testing with "Step test method" is carried out where the load on gear incremented by 5 N for every 15,000 rotations as shown in the Figure 2.23. The testing is performed till the failure of the gear.

Table 2.20: Wear parameters and their levels used during composite development stages

Process parameter	Set value
Load on specimen (kg)	2
Sliding distance (meter)	300
Speed of rotation (rpm)	400
Surface roughness of disk (grit size)	400
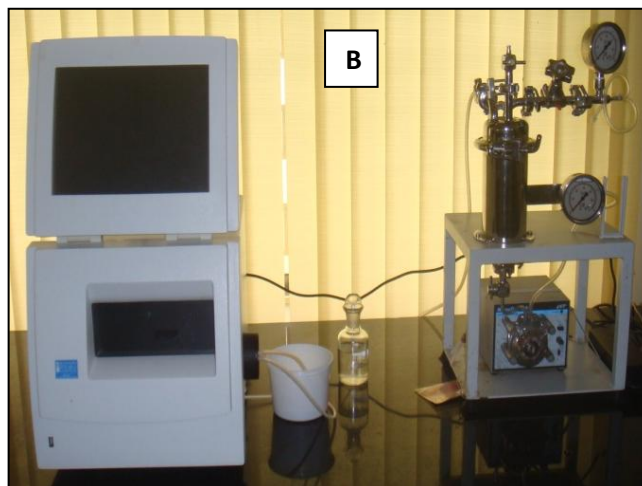
Figure 2.21: FTIR Spectrometer (A) and TGA (B) machines.

Figure 2.22: Test rig for gear testing
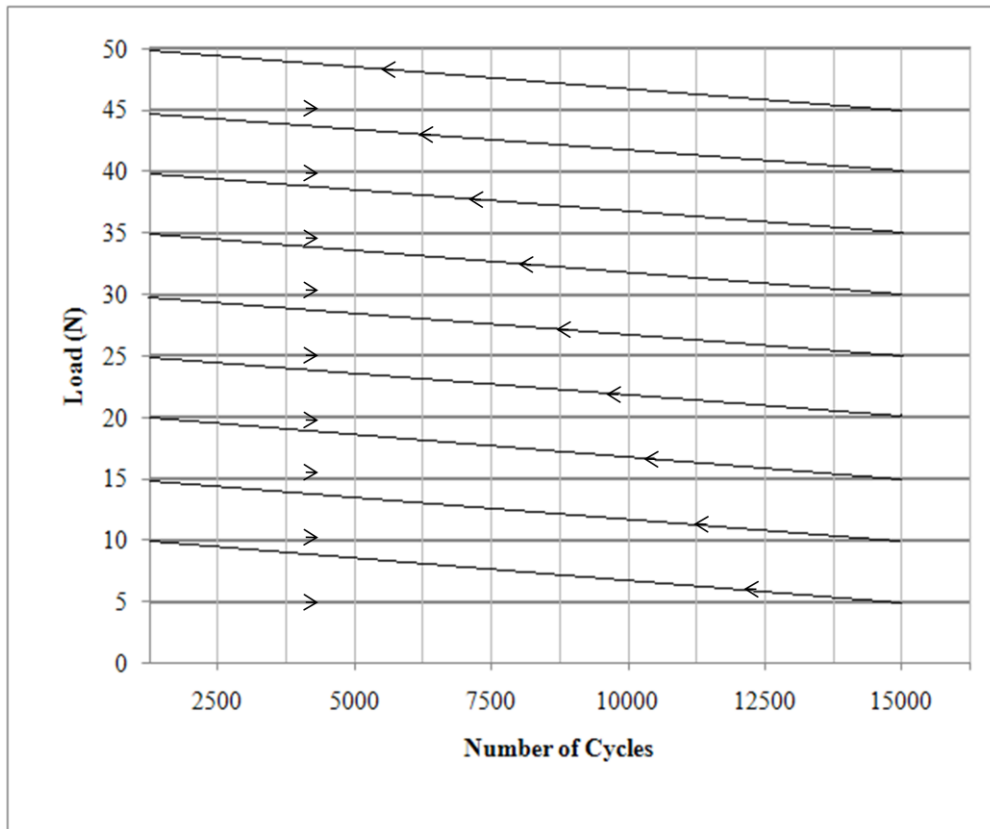
Figure 2.23: Step test procedure followed for testing r-PET/FAC composite gears

(Collins J A 2001)

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CHAPTER 3

RESULTS AND DISCUSSIONS

Motivation to develop a composite material from r-PET with FAC as reinforcement in applications such as gears, derived from the literature survey, is presented in chapter one. The second chapter details the properties of the materials involved, experimentation and testing procedures adopted. In the present chapter the results of the study made on compression moulding of r-PET/FAC composites, to meet the objectives specified in chapter one, is presented. The results of the experimentation are put forth in five stages in the current chapter.

Stage one (Section 3.1) provides results of DMADV procedure followed for developing the moulding process for r-PET. The second stage (Section 3.2) details the results of DOE conducted for r-PET/ FAC composite. The third stage presents the results of matrix blending and treating of reinforcement (Section 3.3, to 3.7). Results of compression moulding optimization using Six Sigma DMAIC procedure and confirmatory experiments are provided in the fourth stage (Section 3.8). The results of testing composite gears moulded using the material developed and optimized parametric settings are dealt at the end of this chapter (Section 3.9).

3.1 RESULTS OF DEVELOPING COMPRESSION MOULDING FOR R-PET

Six Sigma DMADV tool is adopted to develop a moulding process for post consumer PET. The initial steps viz. define, measure and design are detailed in the chapter two (section 2.3.1). The results of the experimentation conducted on the basis of L_{16} orthogonal array and subsequent processes carried out to develop the process are provided in this section.

Verify

In this stage of Six Sigma DMADV implementation, the experimental plan designed for compression moulding r-PET is verified through pilot runs.

a. Results of Pilot Runs

The results obtained on the quality of the samples moulded using L_{16} OA, charging the mould with r-PET flakes are presented in the Table 3.1. The quality of moulded samples can be broadly classified into four categories, viz. a. incomplete melting, b. large void formation, c. small void formation and d. char formation.

Table 3.1: Results of compression moulding flakes of r-PET

Expt. No.	Moulding Time (Min)	Moulding Press(kg/cm^2)	Moulding Temp. (˚C)	Sample Quality
1	4	25	250	Incomplete melting
2	4	50	260	Large Voids
3	4	75	270	Small Voids
4	4	100	280	Char formed
5	6	25	260	Large Voids
6	6	50	250	Incomplete melting
7	6	75	280	Char formed
8	6	100	270	Small Voids
9	8	25	270	Small Voids
10	8	50	280	Char formed
11	8	75	250	Incomplete melting
12	8	100	260	Large Voids
13	10	25	280	Char formed
14	10	50	270	Small Voids
15	10	75	260	Large Voids
16	10	100	250	Incomplete melting

From the data in Table 3.1, it could be inferred that moulding temperature is one of the key parameters. Moulding PET at temperatures up to 250˚C, lead to the retention of raw material in its original form (flakes) without proper binding. At temperatures higher than 280˚C the flakes get decomposed leading to char formation while the intermediate

temperatures tend to form large voids in the sample. The FMEA worksheet for large void formation is shown in the Table 3.2.

Table 3.2: FMEA Worksheet for the formation of Large Voids in moulded r-PET

Func-tion	Failure Mode	Effects	Severity Rating (S)	Causes	Occurr-ence Rating (O)	Current Controls	Detection Rating (D)	Risk Priority Number (RPN)	Recommended Action	Action Taken
Three Point Bending sample	Large voids are formed	Poor quality	9	Large grain size of the flakes	10	Granu-lated flakes are used	10	900	Reduce grain size of flakes	Flakes grinded

The process of moulding r-PET using flakes of r-PET leads to RPN as high as 900. One of the necessary actions could be to reduce the size of r-PET flakes. A grinder is used to powder the flakes. Experiments, to verify the correctness of the action taken, are conducted using r-PET powder. The samples displayed smaller voids (Figure. 3.1).
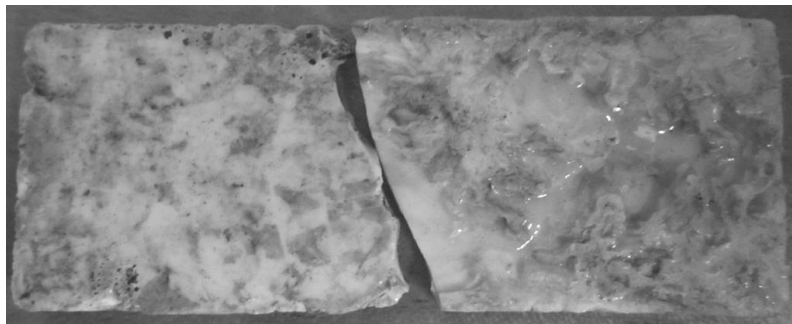
Figure 3.1: Fragile sample with small voids, moulded using r-PET powder.

On reducing the size of the flakes, the size of voids reduced with appreciable decrease in RPN to 315. The FMEA work sheet for redesigned process is in Table 3.3. Based on this observation, the action decided is to convert r-PET powder into a mushy charge. In this direction, the PET powder is heated to convert it in to a mushy charge before loading into the mould cavity.

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Table 3.3: FMEA Worksheet for Small Void Formation in r-PET samples

Func-tion	Failure Mode	Effects	Severity Rating (S)	Causes	Occurr-ence Rating (O)	Current Cont-rols	Detec-tion Rating (D)	Risk Priority Number (RPN)	Recomm-ended Action	Action Taken
Three Point Bending sample	Small voids are formed	Poor quality	9	Medium grain size of the flakes	7	Ground powder is used	5	315	Convert powder to dough moulding compound DMC/BMC	Powder is converted to dough moulding compound

On loading r-PET charge to the mould in mushy form, PET flows adequately, reduces air entrapment and hence, formation of voids in the moulded sample. The FMEA work sheet for void formation after developing compression moulding process for r- PET is tabulated in Table 3.4.

Table 3.4: FMEA Worksheet for Void formation

Func-tion	Failure Mode	Effects	Severity Rating (S)	Causes	Occurr-ence Rating (O)	Current Cont-rols	Detec-tion Rating (D)	Risk Priority Number (RPN)	Recomm-ended Action	Action Taken
Three Point Bending sample	Voids are formed	Poor quality	2	Grain size of the flakes	2	DMC/ BMC is used	2	8		Problem Solved

Loading the mould by converting r-PET powder into mushy charge, RPN is found to reduce from 315 to 8. Such a procedure of moulding produces fairly good samples, as shown in the Figure 3.2.

In order to investigate the effects of mechanical recycling, Fourier Transformation Infra Red Spectroscopy (FTIR) is conducted on r-PET samples before and after processing. The spectrograms are shown in Figures 3.3 and 3.4 respectively. Comparison of the results with the absorption wave numbers for the functional groups like C-O, C=O and C-H, show that the functional groups are intact in the polymer even after moulding,

indicating signs of little degradation (Changqing et al. 2006). The extended peak in the r-PET powder at 2358 cm^{-1}, could be due to the CO_2 entrapped between the powder granules and is not specifying to any functional group of the polymer.

Figure 3.2: Fairly good sample moulded using the process developed.
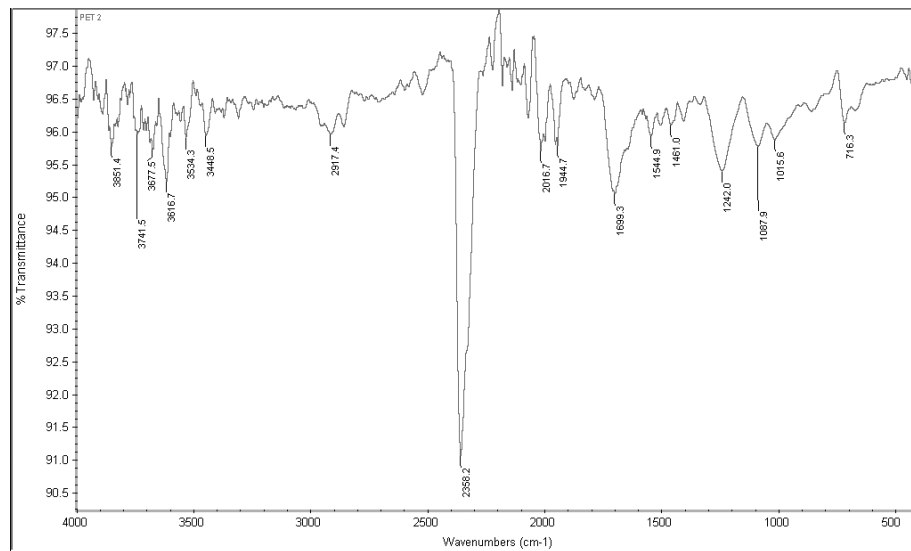
Figure 3.3: FTIR spectrogram of r- PET powder

After developing such a process for moulding r-PET, the polymer is reinforced with FAC. The properties of r-PET/FAC composite are investigated and the results of the studies are provided in the following section.

3.2 RESULTS OF TESTING R-PET/ FAC COMPOSITES

The data collected from flexural and wear tests, using L_{27} OA are analyzed through average values of S/N (ratio of mean to variance) for each factor at three levels and are provided as main effects diagrams in this section. Flexural and wear properties of the composite are presented in the section 3.2.1 and Section 3.2.2 respectively.
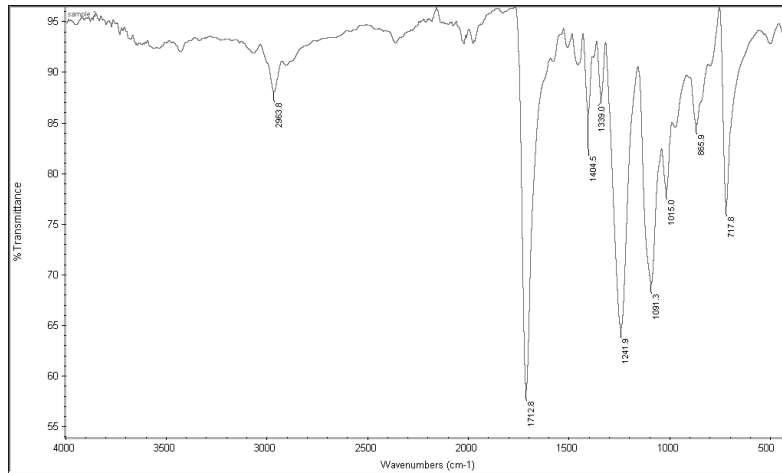
Figure 3.4: FTIR spectrogram of compression moulded r-PET sample

3.2.1 Flexural properties of r-PET/FAC composites

The flexural test data collected for experiments conducted based on L_{27} OA (Table 2.14) is presented in the Table 3.5. These data are used to analyze the effect of process and material parameters on the flexural properties of r-PET composite. The flexural properties under consideration are flexural strength, fracture strain, toughness and elastic modulus. Since these properties are the case of higher the better, the objective function (S/N ratio) to be maximized given in the form of equation 1.8 in Section 1.8.3 is taken. The mean S/N ratio is computed for all 27 experiments and they are tabulated in the Table 3.6.

Analysis of mean S/N ratio

The average values of S/N ratios for each factor at levels 1 to 3 are represented in the response table (Tables 3.7 to 3.10). The corresponding main effects diagram is displayed in Figures 3.5. to 3.8. The term delta in the response tables represents the criticality of the factor for the response and it is the difference between the extreme values of S/N. This can also be represented as a rank of the factor. Higher rank implies that the factor is more critical to quality. It can be observed from the response table that FAC content in the composite is the most critical factor and the moulding pressure and the temperature are the next best factors. The moulding time and mould cooling types are of less significant. The results suggest that careful selection of the FAC content, pressure and temperature is essential while moulding r-PET composite as they can alter the response considerably.

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Table 3.5: Flexural test results of r-PET/FAC composites

Expt No.	Mean flexural strength (MPa)	Mean fracture strain (%)	Mean toughness (kJ/m^3)	Mean flexural modulus (MPa)
1	17.13	0.76	65219	2990
2	15.27	0.76	57925	3253
3	16.50	0.62	51490	3295
4	16.34	0.82	67317	3168
5	13.54	0.63	42851	3465
6	19.49	0.75	73338	3450
7	13.19	0.64	42299	3003
8	22.67	0.81	92071	3507
9	16.48	0.75	61632	3194
10	14.94	0.80	59441	2751
11	22.36	0.78	86691	2330
12	16.67	0.68	57065	3130
13	22.35	0.87	96994	2410
14	16.29	0.74	60175	3060
15	14.19	0.78	55029	2649
16	17.03	0.80	68233	2849
17	15.53	0.77	59513	2613
18	22.11	0.79	87758	2414
19	17.77	0.76	67252	2230
20	15.31	0.71	54421	2935
21	22.76	0.89	101177	2244
22	15.92	0.74	58755	2793
23	23.32	0.96	111843	2190
24	18.87	0.71	67178	2458
25	22.53	1.06	119392	2230
26	19.09	0.76	72188	2407
27	14.02	0.69	48051	3010

Table 3.6: Mean S/N ratios calculated for the flexural properties

Expt. No.	S/N ratio (flexural strength)	S/N ratio (fracture strain)	S/N ratio (toughness)	S/N ratio (flexural modulus)
1	24.675	-2.384	96.287	69.513
2	23.677	-2.384	95.257	70.246
3	24.350	-4.152	94.234	70.357
4	24.265	-1.724	96.562	70.016
5	22.632	-4.013	92.639	70.794
6	25.796	-2.499	97.307	70.756
7	22.405	-3.876	92.527	69.551
8	27.109	-1.830	99.282	70.899
9	24.339	-2.499	95.796	70.087
10	23.487	-1.938	95.482	68.790
11	26.989	-2.158	98.759	67.347
12	24.439	-3.350	95.127	69.911
13	26.986	-1.210	99.735	67.640
14	24.238	-2.615	95.588	69.714
15	23.040	-2.158	94.812	68.462
16	24.624	-1.938	96.680	69.094
17	23.823	-2.270	95.492	68.343
18	26.892	-2.047	98.866	67.655
19	24.994	-2.384	96.554	66.966
20	23.700	-2.975	94.715	69.352
21	27.143	-1.012	100.102	67.020
22	24.039	-2.615	95.381	68.921
23	27.355	-0.355	100.972	66.809
24	25.515	-2.975	96.545	67.812
25	27.055	0.506	101.540	66.966
26	25.616	-2.384	97.169	67.630
27	22.935	-3.223	93.634	69.571

Table 3.7: Response table for flexural strength in terms of mean S/N ratio

Level	Pressure (MPa)	Time (Min.)	Cooling type	Temperature (˚C)	FA Cenosphere (%)
1	24.36	24.83	24.73	24.62	26.67
2	24.95	24.87	25.02	24.91	24.63
3	25.37	24.98	24.94	25.15	23.38
Delta	1.01	0.15	0.29	0.54	3.26
Rank	2	5	4	3	1
Significance	Very Significant	Less Significant	Less Significant	Significant	Very Significant
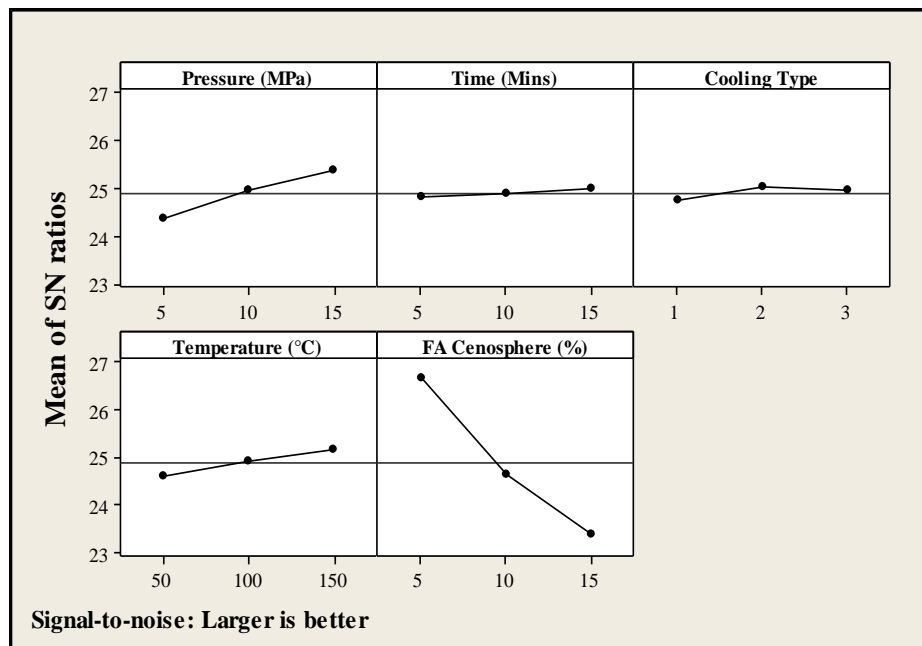
Figure 3.5: Main effects for flexural strength of r-PET/FAC composite in terms of S/N ratio

From the main effects diagram for flexural strength, the optimum levels of parameters are found as moulding pressure (A3), moulding time (B3), mould cooling (C2), moulding temperature (D3), and FA Cenosphere (E1), respectively.

Similar analysis of S/N ratio for fracture strain, toughness and modulus are provided in the following tables

Table 3.8: Response table for fracture strain in terms of mean S/N ratio for r-PET/FAC composite

Level	Pressure (MPa)	Time (min)	cooling type	Temperature (°C)	FA Cenosphere (%)
1	-2.19	-2.53	-1.95	-2.60	-1.44
2	-2.19	-2.24	-2.33	-1.54	-2.47
3	-1.94	-2.17	-2.66	-2.80	-3.03
Delta	0.88	0.35	0.71	1.26	1.58
Rank	3	5	4	2	1
Significance	Significant	Less Significant	Less Significant	Very Significant	Very Significant
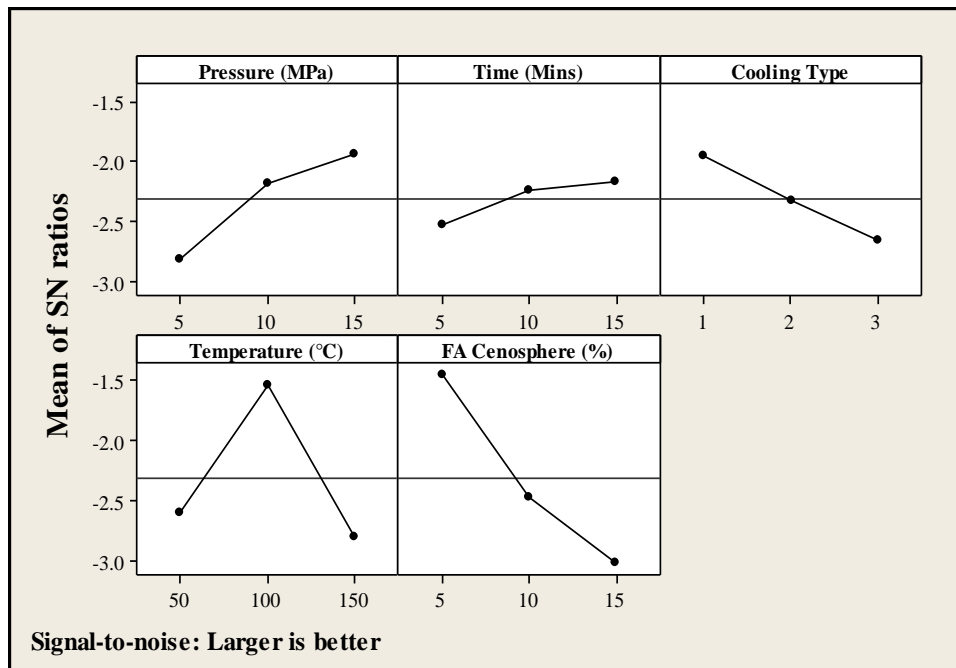
Figure 3.6: Main effects in terms of S/N ratio for fracture strain

From Figure 3.6 the optimum levels of parameters are found as moulding pressure (A3), moulding time (B3), mould cooling (C1), moulding temperature (D2), and FA Cenosphere (E1), respectively for the fracture strain.

Table 3.9: Response table for toughness in terms of mean S/N ratio

Level	Pressure (MPa)	Time (min)	Cooling type	Temperature (˚C)	FA Cenosphere (%)
1	95.54	96.28	96.75	96.00	99.21
2	96.73	96.62	96.65	97.34	96.14
3	97.40	96.78	96.27	96.34	94.32
Delta	1.86	0.50	0.48	1.33	4.88
Rank	2	4	5	3	1
Significance	Very Significant	Less Significant	Less Significant	Significant	Very Significant
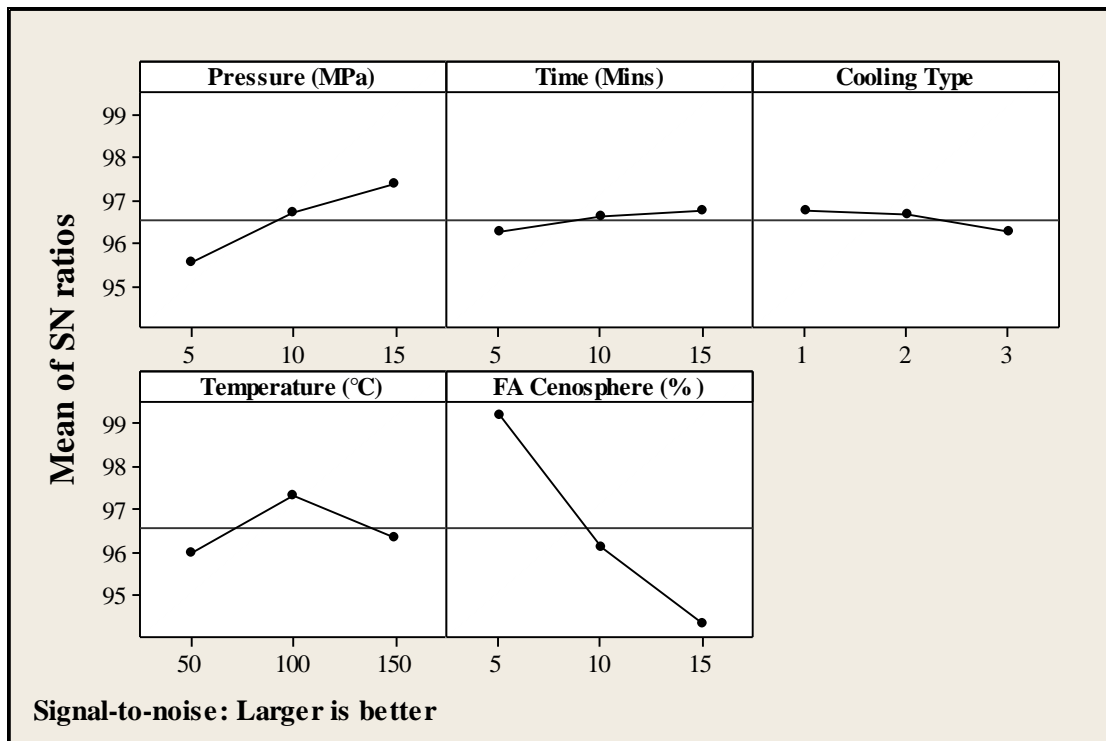
Figure 3.7: Main effects diagram for toughness

Optimum levels of parameters from Figure 3.7 for the toughness are found as moulding pressure (A3), moulding time (B3), mould cooling (C1), moulding temperature (D2), and FA Cenosphere (E1), respectively.

Table 3.10: Response table for modulus of r-PET/FAC composite in terms of mean S/N ratio

Level	Pressure (MPa)	Time (min)	cooling type	Temperature (°C)	FA Cenosphere (%)
1	70.25	68.83	68.61	69.75	68.29
2	68.55	68.99	69.01	68.53	69.05
3	67.89	68.87	69.07	68.42	69.35
Delta	2.35	0.16	0.46	1.33	1.06
Rank	1	5	4	2	3
Significance	Very Significant	Less Significant	Less Significant	Very Significant	Significant
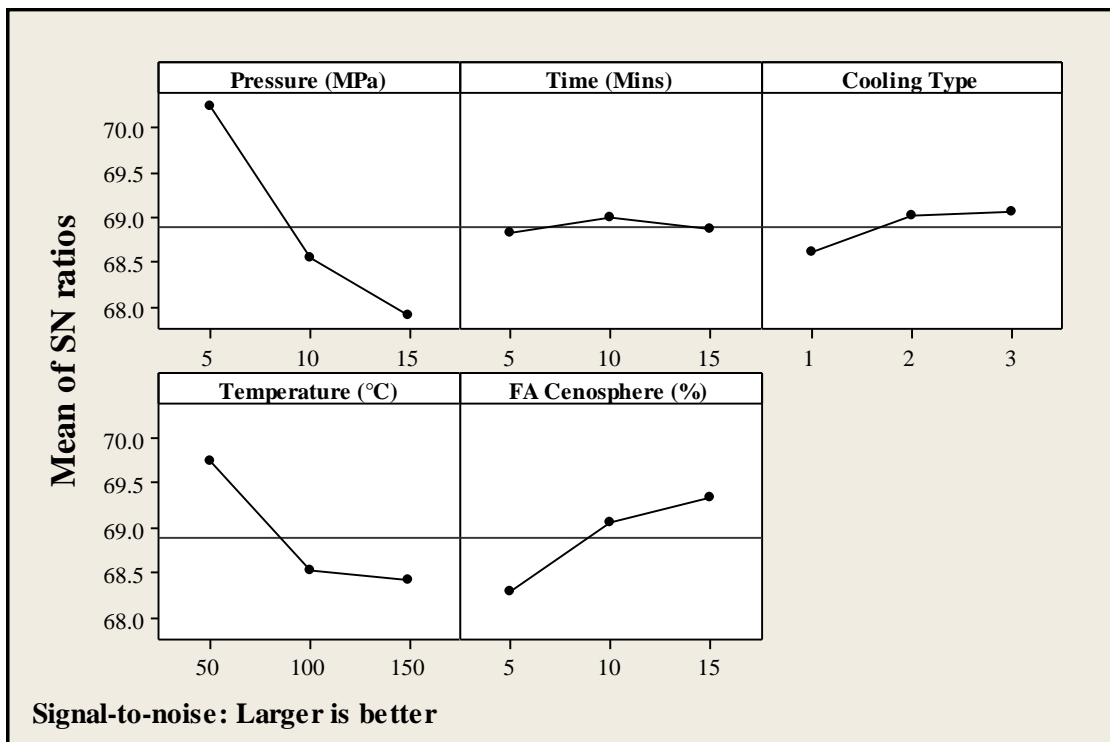
Figure 3.8 Diagram displaying main effects for modulus

The parametric settings for elastic modulus are found as moulding pressure (A1), moulding time (B2), mould cooling (C3), moulding temperature (D1), and FA Cenosphere (E3), respectively from Figure 3.6. These collective results on the optimal parametric levels are tabulated in the Table 3.11

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Table 3.11: Compiled data of optimum parameters

Response	Moulding Pressure MPa	Moulding Time min.	Mould cooling type	Moulding Temp. ˚C	FAC Content %
Flexural Strength MPa	15	Less Significant	Less Significant	150	5
Fracture Strain %	15	Less Significant	Less Significant	100	5
Toughness kJ/m^3	15	Less Significant	Less Significant	100	5
Elastic Modulus MPa	5	Less Significant	Less Significant	50	15

3.2.2 Discussion on the results of flexural properties of r-PET/FAC composites

It can be noted from Figure 3.5 to 3.7 that, FAC content in the r-PET composite shows a steep downward trend. The reason could be poor binding between the matrix and the filler. Processing of r-PET/FAC composite is done entirely on a recycling basis without any addition of compatibilizer or surface treatments to FAC. The matrix is organic aliphatic-aromatic polymer and the reinforcing filler is an inorganic alumino-silicate. Such a combination causes poor wetting between the constituents resulting in inferior binding and thus, a poor load sharing. Under stress, differential deformations of matrix and filler lead to formation of new surfaces at the interfaces. A growing micro-crack often prefers these free surfaces as low resistance path for its growth and these free surfaces result in loss of strength (Figure 3.9). Seena Joseph et al. (2010) reported pulling of filler out from the matrix resulting into formation of holes in polymer filled composite, when matrix and reinforcement are not bound properly, under a tensile load. The SEM micrograph of the fracture surface (Figure 3.10 A & B) clearly display the dents formed due to de-bonding of FAC from the matrix.

The improved strength caused by the rise in the moulding pressure can be attributed to reduction in the bulk volume of voids in the composite block. Higher pressures facilitate

escape for entrapped air and gases generated during moulding process reducing the bulk volume of voids. Reduction in the bulk volume at 15 MPa pressure is observed in the SEM micrograph shown in Figure 3.10B. Reduction in the voids reduces the surface available for the cracks to generate and grow. According to Belmonte et al. (2006) presence of air bubbles and voids, which are unavoidable in composites, reduce the strength. The presence of voids on the fracture surface is confirmed in the SEM micrograph, shown in the Figure 3.10A. Although the contribution of mould temperature is low, increase in the temperature provides better flow-ability to the plastic.

3.2.3   Wear properties of r-PET/FAC composites

Nine parameters are considered at three levels in the study of wear behavior of r-PET/FAC composite. The details regarding control process parameters, their levels and the DOE plan are explained in the section 2.3.4. The sample testing for wear properties is explained in section 2.4.2. Specific wear rate (SWR, K_O) is the response considered in this study. Since K_O is a case of lower is better, the objective function selected or the ratio of mean to variance (S/N) to be maximized is taken as in equation 1.7 (Montgomery 1991). The S/N ratios are computed for all 27 experiments and they are tabulated in Table 3.12.
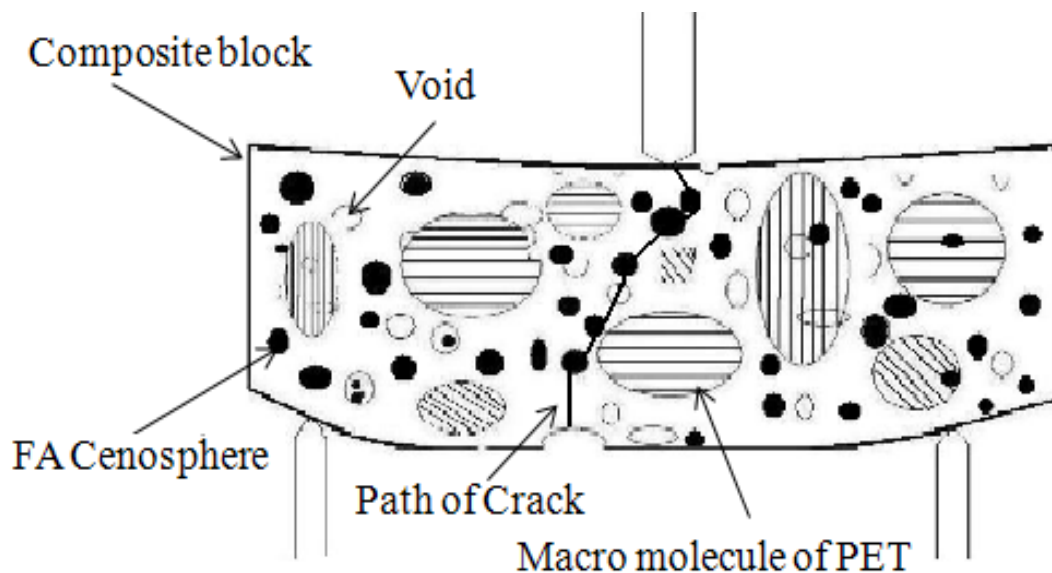
Figure 3.9: Proposed fracture mechanism for r-PET/ FAC composite
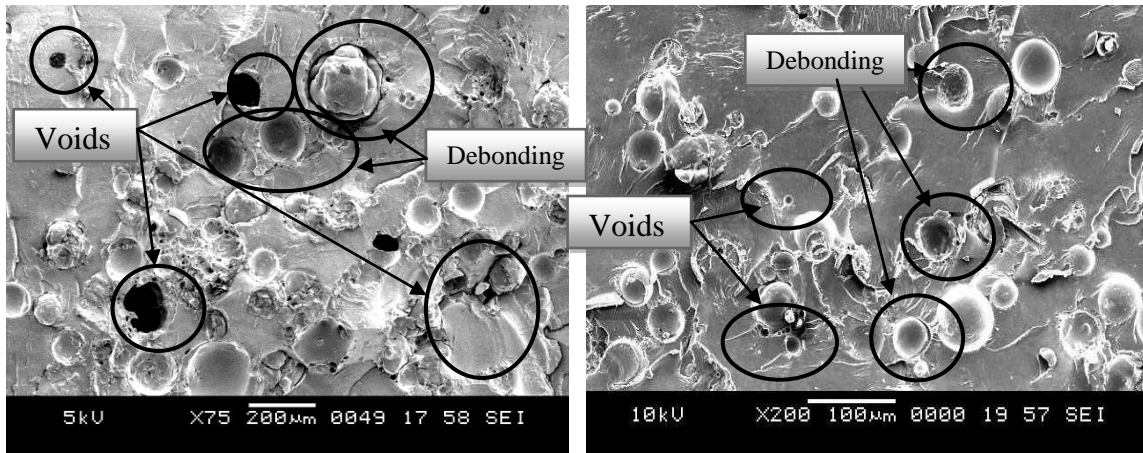
A. r-PET/FAC @ 5 MPa   B. R-PET/ FAC @ 15 MPa

Figure 3.10: SEM pictures showing debonding of FAC from the matrix and reduction in void volume at 15 MPa moulding pressure

The Taguchi method of experimental design is applied for analyzing the significance of individual parameters and their optimum levels for achieving a minimum wear rate. The mean values of S/N ratios for each parameter at levels 1−3 are illustrated in Table 3.13.

Table 3.12: Experimental results of SWR and their corresponding S/N ratio

Expt No.	Mean Wt. Loss $*10^3$ (kg)	Mean Density (kg/m^3)	Specific wear rate K_O $*10^{-12}$ (m^3/Nm)	Mean S/N
1	0.01155	1203.6	6.521	223.713
2	0.00838	1250.0	4.556	226.828
3	0.00516	1741.3	2.014	233.919
4	0.00778	1473.4	0.897	240.942
5	0.00661	1147.5	0.979	240.187
6	0.04636	1199.7	6.565	223.654
7	0.01375	1490.7	0.696	243.141
8	0.05136	1585.3	2.446	232.230
9	0.22700	1340.6	12.785	217.865
10	0.08022	1320.0	6.883	223.243
11	0.02102	1259.8	1.890	234.471

12	0.00828	1162.2	0.807	241.863
13	0.01368	1365.4	2.270	232.881
14	0.01192	1192.4	2.2646	232.900
15	0.02126	1192.1	4.040	227.872
16	0.00496	1229.0	1.371	237.257
17	0.03468	1161.0	10.150	219.871
18	0.00861	1323.3	2.211	233.109
19	0.07109	1221.5	6.592	223.620
20	0.01676	1232.1	1.541	236.246
21	0.01382	1353.3	1.157	238.736
22	0.02136	1185.1	4.083	227.781
23	0.00690	1209.3	1.293	237.771
24	0.05778	1430.9	9.148	220.774
25	0.00764	1660.6	1.563	236.119
26	0.03148	1331.5	8.033	221.902
27	0.01660	1322.0	4.267	227.398

Table 3.13: Mean value of S/N ratio for SWR at each level

Level	Moulding pressure A	Moulding time B	Load on specimen C	Sliding distance D	Mould Cooling type E	Speed of rotation F	Roughness of surface G	Moulding temperature H	FA Cenosphere I
1	233.6	231.4	299.0	229.3	232.3	234.2	224.1	231.4	232.5
2	231.5	231.6	232.2	232.2	231.4	231.1	233.1	232.2	231.6
3	230.0	232.1	233.9	233.2	231.7	230.0	238.0	231.6	231.1
Delta	3.6	0.7	4.9	3.9	0.9	4.2	13.9	0.8	1.4
Rank	5	9	2	4	7	3	1	8	6
Optimum Level	15	Not significant	1	150	Not significant	600	220	Not significant	15

From the response table (Table 3.13), the optimum levels of moulding parameters are found to be moulding pressure (A3), moulding time (B1), mould cooling (E2), moulding temperature (H1), and weight fraction of FAC C (I3). Similarly the optimum levels of wear parameters are Load on specimen (C1), sliding distance (D1), speed of rotation (F3)

and surface roughness (G1). The significance ranking and optimum levels for the test parameters are also detailed in the Table 3.13. An insight in to the results of experimentation points to the facts that the wear parameters are prominent (rank 1 to 4) than the moulding parameters (rank >4) in deciding the wear rate of the r-PET composite. Further, for a detailed analysis of wear behaviour of r-PET composites, a separate study on the responses for wear and moulding parameters is carried out. The significance ranking for wear parameters in descending order is surface roughness, load on the specimen, rotational speed of the disk and sliding distance. These observations seem similar to those available in the literature (Kishore et al. 2001, Hasim et al. 2002, Jia et al. 2007).

The response graph of the moulding and material parameters is shown in Figure 3.11. Moulding pressure and the weight fraction of FAC are found to be more significant to the wear than the moulding temperature, time and cooling type. Further, pressure and cenosphere content display a downward trend suggesting higher values for production (15MPa, 15%).
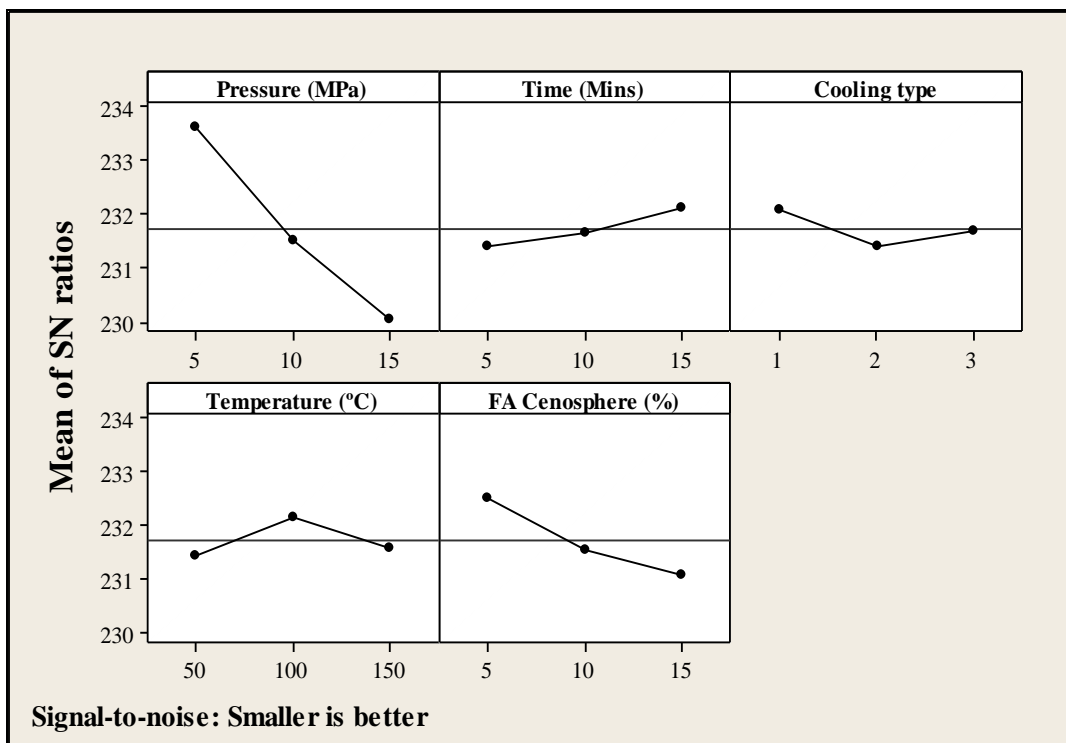
Figure 3.11: Main effects in terms of S/N ratio for Specific wear rate
(Moulding Parameters)

90

3.2.4 Discussion on the results of wear properties of r-PET/FAC composites

The effect of moulding, material and wear parameters on the wear rate of r-PET/FAC composite can be explained as follows. The drop in wear rate at higher pressures can be explained in terms of the void formation and filling up of voids by FAC. According to Belmonte et al. (2006) presence of air bubbles and voids, which are unavoidable in composites, reduce the strength and facilitates wear. Further, they initiate the cracks in the composite and cause expulsion of material. At higher pressure, chances of void formation are less as the charge is better compacted. Further, fillers occupying the voids reduce bulk volume of voids. Figure 3.11 also depicts a downward gradient for FAC content. When r-PET is rubbed against a rough counter face, the hard SiC particles of counter face tears the material from the specimen leading to the weight loss. The loss is predominant at higher loads as the existing tearing forces are higher in magnitude. The improved wear property of the composite for higher proportions of FAC could be due to the multiple properties of FAC. They are hard, hollow spherical alumino-silicates with high compressive strength. In absence of these particles, the resistance offered by the wearing material is less, as r-PET is exposed to a temperature above its glass transition temperature. The lower strength of r-PET above Tg resists less to the tearing force leading to higher wear loss (Figure 12A). In the SEM picture shown in Figure 3.13A a smooth wear surface confirms lower resistance for material loss. In the composite FAC prevent the matrix from wearing out by offering higher resistance. The increase in the roughness of wear surface owing to an increase in resistance is evident from the Figure 3.13B. At lower loads, the hard spherical surface of the FAC smoothens the movement of the counter face particles, whereas at higher loads the hardness and compressive strength of the filler resists the wearing of the matrix by absorbing the force from the counter face. Further, the worn out composite lumps fill the rough surface of the counter face blunting it to a smooth surface (Figure 3.12B). The blunting of counter face leads to a reduction in wear loss. The magnitude of all these effects is higher at higher concentration of the filler.
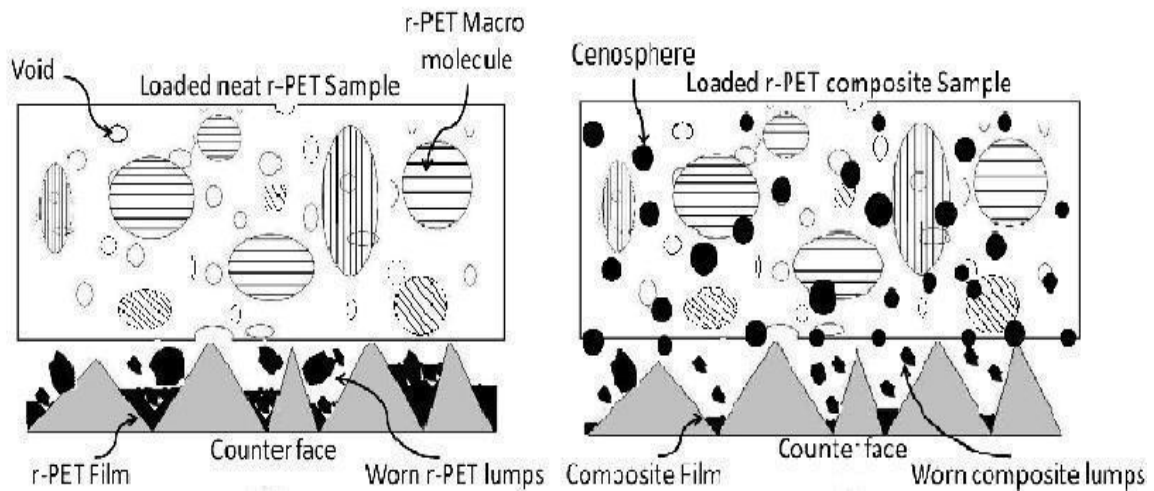
B. Neat r-PET   **B. R-PET/ FAC composite**

Figure 3.12: Proposed wear mechanism for r-PET/ FAC composite
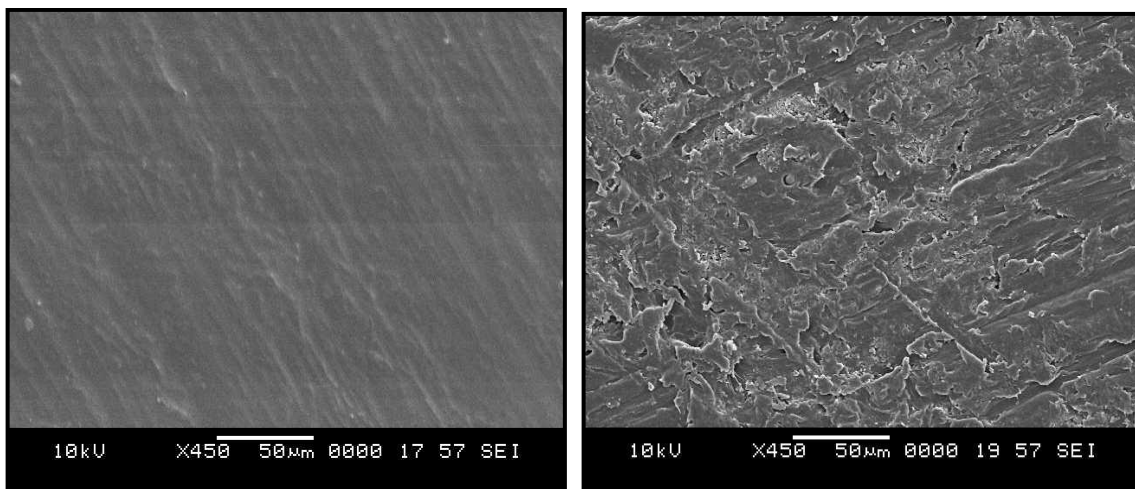
A. Neat r-PET   **B. R-PET/ 15% FAC Composite**

Figure 3.13: SEM micrographs of worn surface of composite

Results of flexural and wear testing of r-PET/ FAC composite reveal that the composites failed to display adequate flexural properties w. r. t. increase in FAC. Brittle nature of matrix and debonding at interface could be observed from fractographic analysis. A brittle matrix often fails to absorb energy required in gearing applications. Hence, modifications that improve the matrix flexibility and reduce debonds are studied in this work. The brittleness is tackled by blending r-PET with softer plastics from recycled arena. Results of these modifications for developing r-PET/FAC composite are provided in the following sections.

3.3 RESULTS OF PRILIMINARY STUDY ON MATRIX BLENDING

Blending matrix with softer plastics is considered in this preliminary study. Five such plastics, as explained in section 2.3.5, are blended with r-PET and the results of experimentation are provided in this section for flexural and wear properties. This exercise is conducted in order to select a suitable blending polymer for r-PET to meet the requirements of the matrix.

3.3.1   Flexural test results of r-PET blends

Flexural strength, fracture strain, toughness and modulus are considered for all the five r-blends. Figure 3.14 (A-D) shows a comparative chart on flexural properties of r-PET blends. The Figure shows that r-LDPE shows highest strength on blending with r-PET both at 10 as well as 30% wt. fraction, whereas r-HDPE at 10% and r-LLDPE at 30% shows least property and the other plastics display intermediate properties. A similar comparison chart for fracture strain is shown in the Figure 3.14B. The improvement in fracture strain at 10% and 30% of blend seems at the peak. The improvement in toughness for r-PET/ r-LDPE blend is observed to be highest of all.
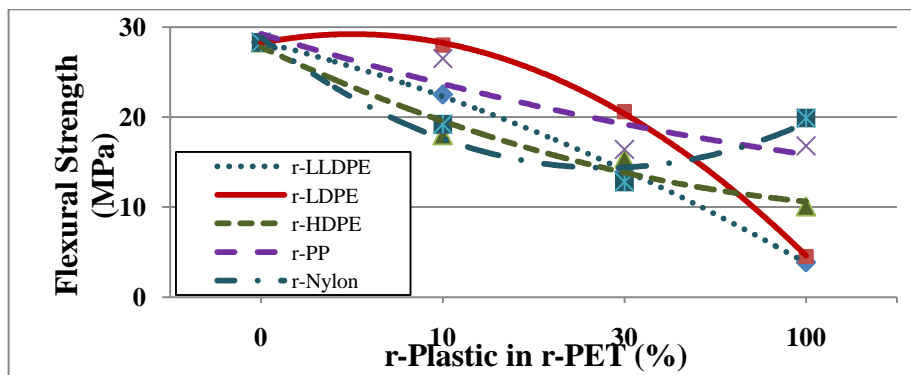
A. Flexural Strength in MPa
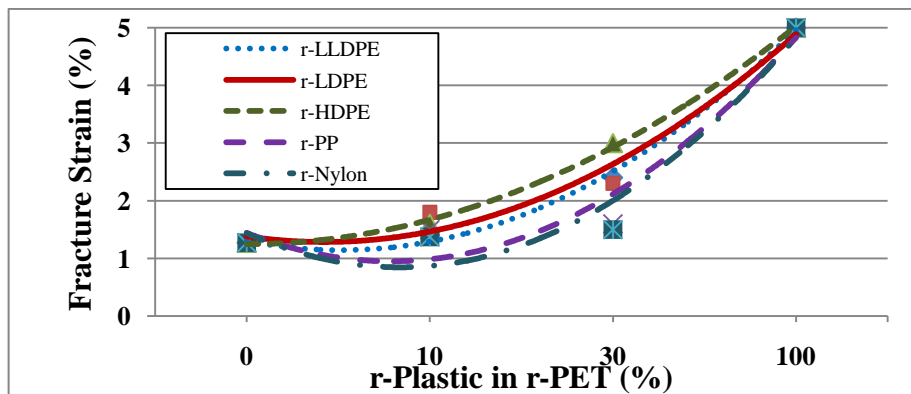
B. Fracture Strain in %
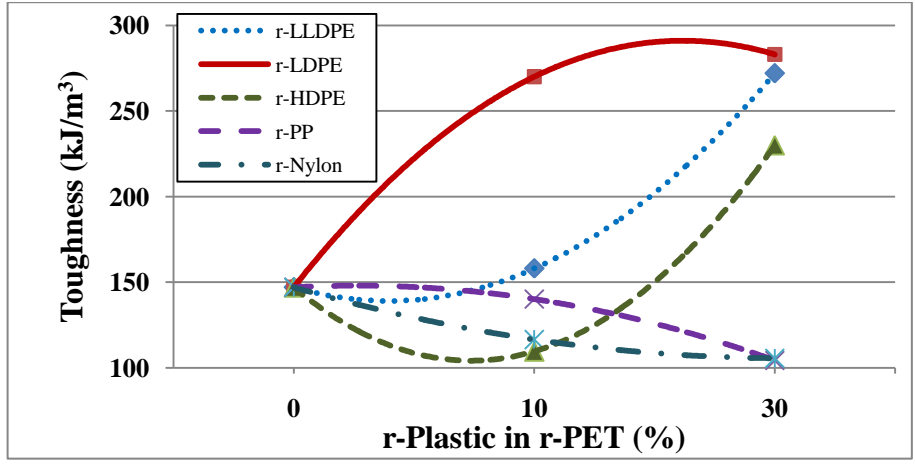
C. Toughness in kJ/m^3
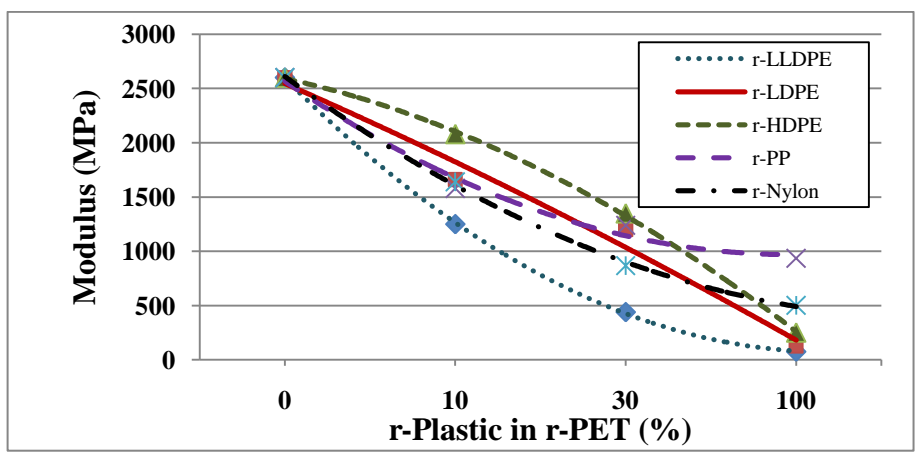
D. Elastic Modulus in MPa

Figure 3.14: Effects of blending plastics on r-PET

The main objective behind conducting these experiments is to reduce the brittleness of the r-PET or to improve the toughness so as to make the material suitable for gears. The area under the stress strain curves is calculated and the resulting comparative chart is shown in the Figure 3.14C. The Figure shows a considerable improvement in the energy absorbing behaviour of r-PET/r-LDPE blend making it a suitable blending plastic for reducing the brittleness of the r-PET. Figure 3.14D displays the modulus of r-PET blends. Substantial drop in the modulus of r-PET blends indicate improvement in the flexibility of the blends.

These results leads to the fact that r-LDPE could be a better blend for r-PET in comparison to any other plastics considered in this work. The stress strain diagram for r-PET/r-LDPE blend is shown in the Figure 3.15. The Figure 3.15A is the stress strain diagram for the neat r-PET and 3.15D is that for neat r- LDPE. Figure 3.15B and 3.15C are the said diagrams for the blends with 10% and 30% weight of the r-LDPE respectively. These Figures show gradual decrease in the modulus with increase in blending plastic. Further, transformation of the brittle material (neat r-PET) into a tougher material (30% r-LDPE) is also evident from the Figures. Further, improvement in the plasticity of the blend is observed in SEM micrographs of the blend. Figure 3.16A shows the SEM picture of r-PET blended with 10% r-LDPE. The Figure is a proof for plastic rupture at the fracture surface. An increase in plasticity with rise in r-LDPE content in the blend is evident from Figure 3.16B. This Figure depicts SEM microgram for r-PET blend with 30% r-LDPE. The pictures clearly indicate possibilities for improvements in fracture strain of the blends observed during flexural tests.
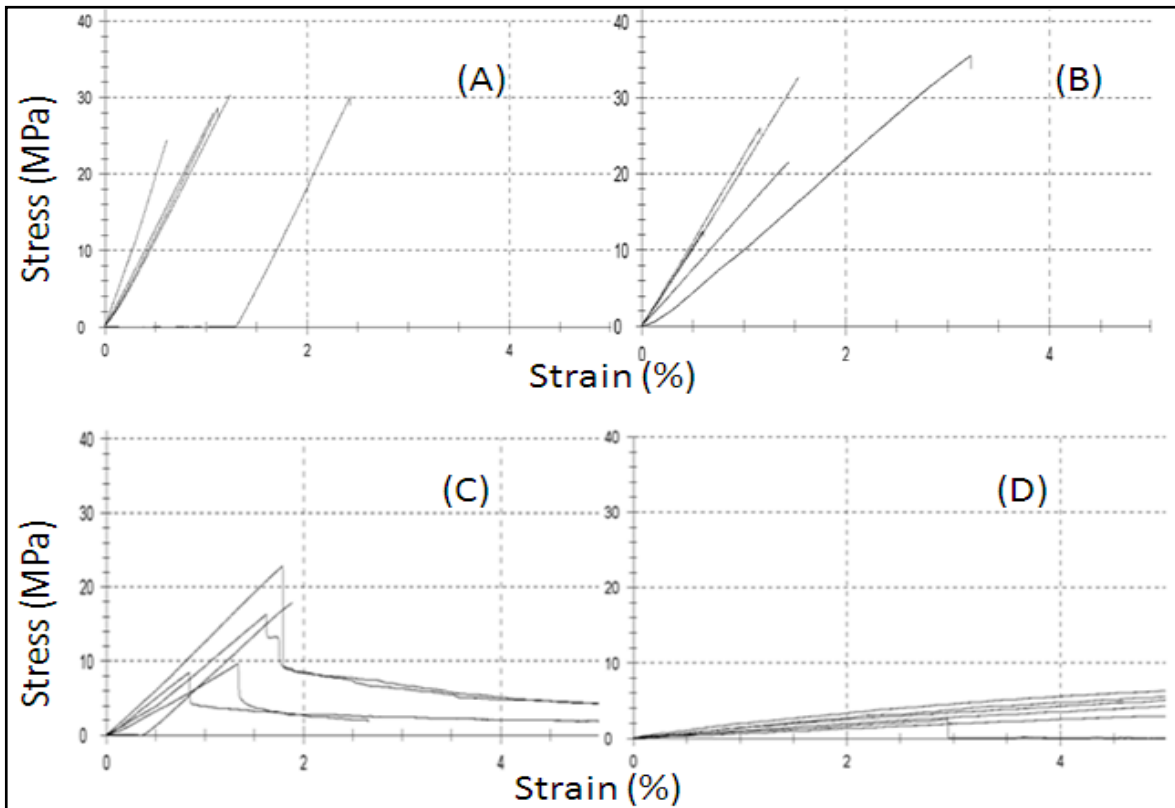
Figure 3.15: Stress strain diagrams for r-PET/LDPE blends

A. Neat r-PET, B. 10% r-LDPE blend, C. 30% r-LDPE blend, D. neat r-LDPE.
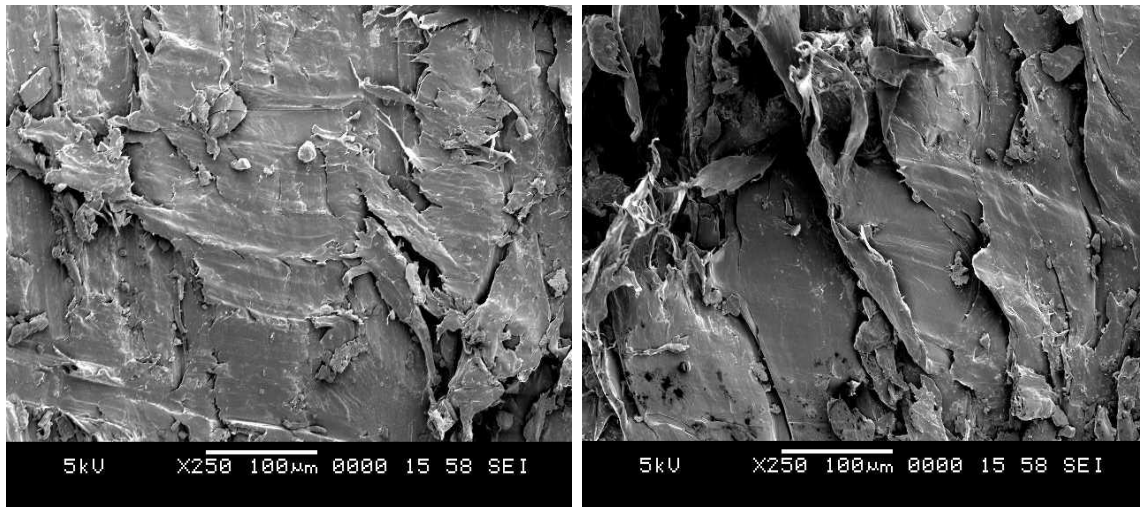
A. 10% r-LDPE   **B. 30% r-LDPE**

Figure 3.16: SEM micrographs of r-PET/r-LDPE blends (M-r-PET)

3.3.2 Wear properties of r-PET blends

The r-PET blend is also tested for their wear behavior to facilitate proper selection of a blending plastic for r-PET. Figure 3.17 shows a comparative plot of wear data on r-PET blended with r-LLDPE, r-LDPE, r-HDPE, r-PP and r-Nylon respectively. The results reveal that the wear loss increases with an increase in the proportion of blending plastic. Neat r-PET shows lower weight loss and blending it with softer plastics increases the weight loss. This reveals that r-PET blends have an upward gradient indicating more weight loss at higher proportions of blending plastics. However there is an exception for r-PET/r-Nylon blend which shows higher weight loss at 30% proportion than that for the neat r-Nylon.

In order to visualize a clear picture about the wear behaviour of the blends and to choose an appropriate blend for r-PET, specific wear rate K_o in m^3/Nm is used as a criteria. Figure 3.18 shows a comparative plot of specific wear rate for r-PET blends at different compositions of blending plastics. The results indicate that r-LDPE displays minimum specific wear rate both at 10 % and 30% concentration where as r-PP has higher values. The other recycled blends display intermediate results.
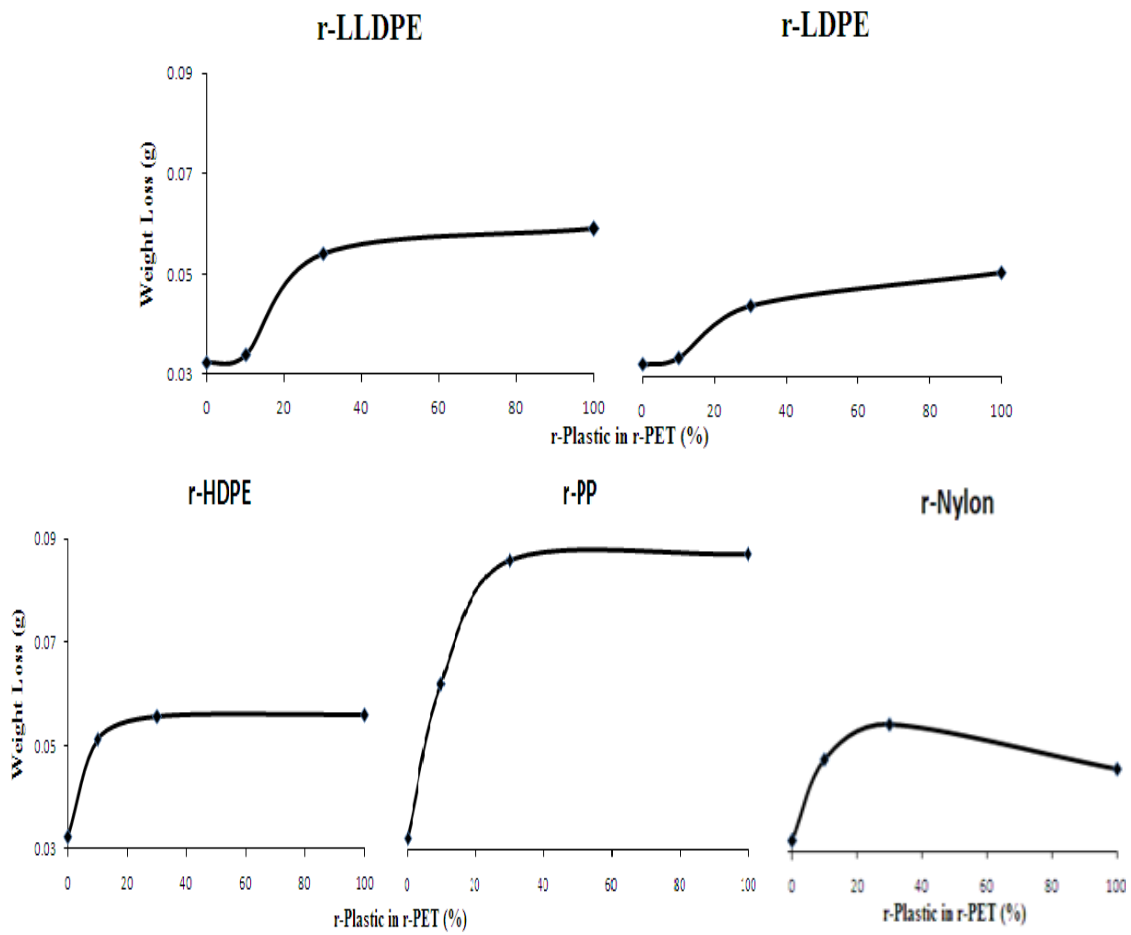
Figure 3.17: Wear data of r-PET blends.
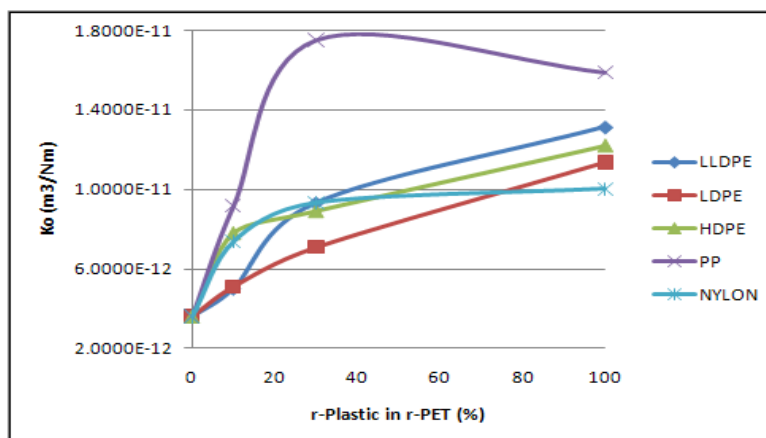
Figure 3.18: Specific Wear rates of r-PET blends

The study on flexural and wear behavior of r-PET blends demonstrates that r-LDPE marginally affects the strength and wear rate. The improvement in toughness and drop in

modulus makes it a suitable blending polymer for r-PET matrix. In the following section the effect of r-LDPE on the r-PET/ FAC composite (M-r-PET/FAC) is presented.

3.4   RESULTS OF TESTING M-r-PET/ FAC COMPOSITE

The matrix is modified with r-LDPE and the properties of M-r-PET/FAC composite are given in the following sections. Section 3.4.1 presents flexural properties and the wear properties are in sections 3.4.2.

3.4.1   Flexural properties of M-r-PET/FAC composites

Flexural strength, fracture strain, modulus and toughness are the properties considered in this study. Figure 3.19 shows the performance of r-LDPE blended composite at 10, 20 and 30% by weight of r-LDPE. It can be noted from the figures that addition of FAC reduces all flexural properties except modulus in the absence of r-LDPE. This can be attributed to poor binding of filler to the matrix leading to easy passage for crack propagation, as explained in the section 3.2.2. FAC being a high modulus ceramic, improvement in the modulus of the composite is as expected. R-LDPE being a low modulus plastic, blending it with the matrix reduces the modulus.

Tests on matrix modifications indicate a marginal, drop in the strength. However, an improvement in the fracture strain is noted. R-LDPE being more rubbery when compared to r-PET, improves the strain-ability of the composite. Improvement in toughness of the blended composite (Figure 3.19C) could also be seen.

Blending r-PET lead to a decrease in the modulus (Figure 3.19D) thus, reducing brittleness. Improvement in the plasticity of the matrix is observed in M-r-PET/FAC composites owing to blending but debonding of FAC particles as observed in Fig. 3.20 could be the reason for decrease in the Flexural strength. Further, increase in FAC content in blended composite lead to a drop in strain as well as toughness. Developing the composite, with an intention to enhance the flexural strength, requires binding FAC to the matrix. Such a study on treated filler is elaborated in the section 3.5.

A. Flexural Strength in MPa

B. Fracture Strain in %

C. Toughness in kJ/m³

D. Elastic Modulus in MPa
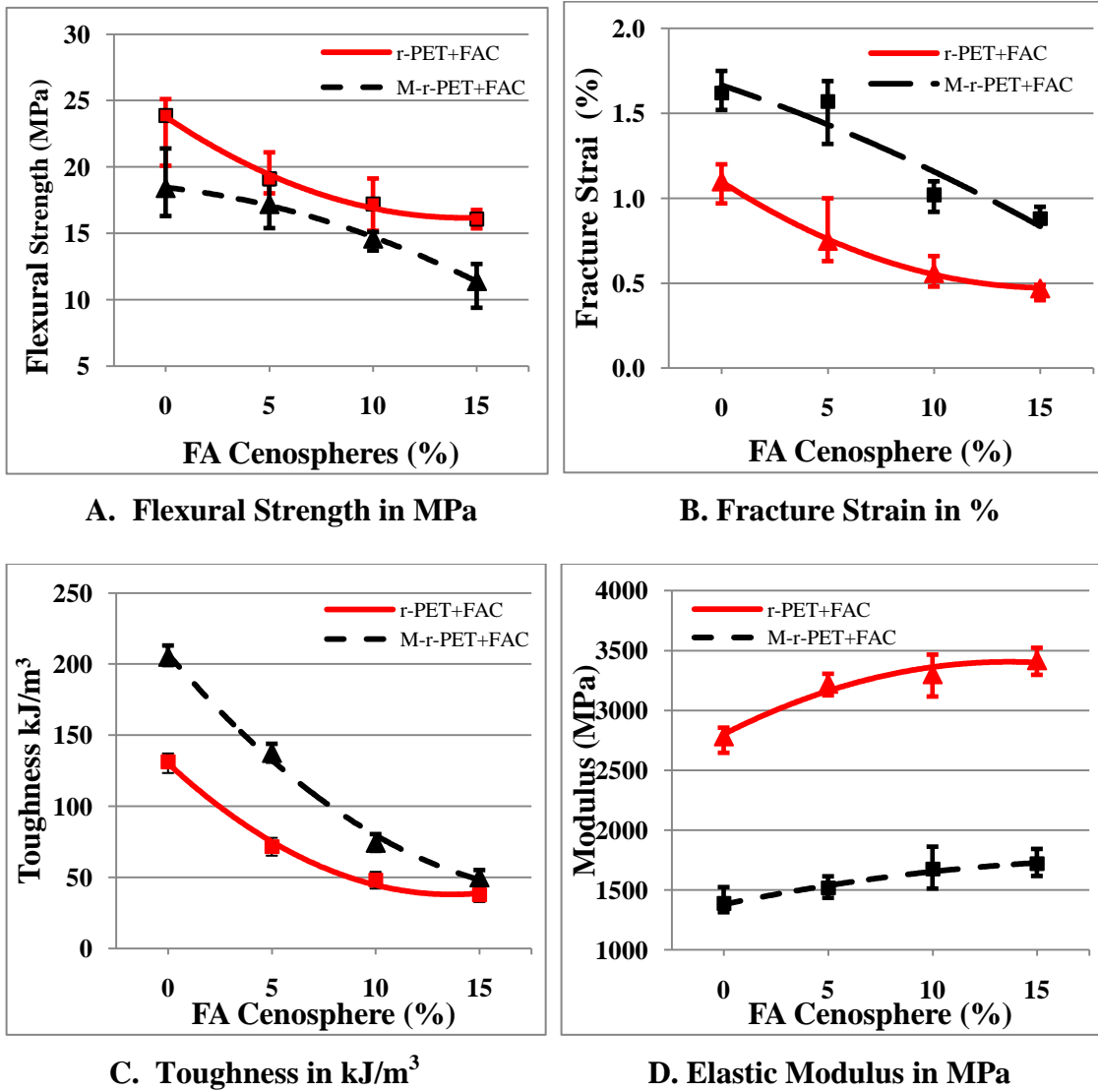
Figure 3.19: Effects of blending on the flexural properties of r-PET/FAC composites
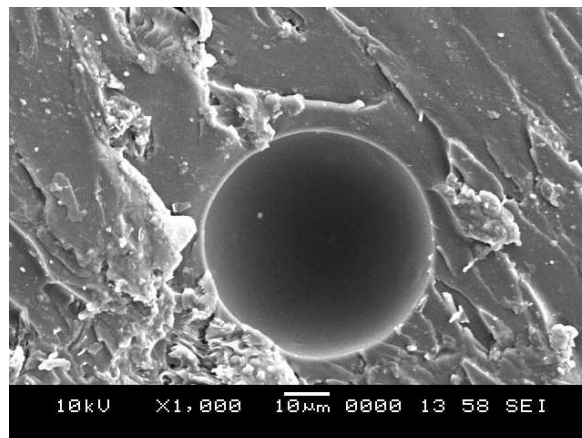
Figure 3.20: Fracture surface of M-r-PET/FAC composite showing debonded FAC

in the plastic matrix

3.4.2 Wear test results of M-r-PET/FAC composites

Figure 3.21 displays the wear properties of M-r-PET/FAC in comparison to r-PET/FAC composites. The SWR of matrix modified composite is lower than r-PET/FAC composite. A 39% decrease in the specific wear rate of the composite is observed at 5% FAC and 19% at 15% FAC (Figure 3.21). Addition of r-LDPE marginally reduces the wear rate of r-PET by about 10%, however, reinforcing blended matrix increases the wear rate by 23% at 15% FAC. A maximum of 53% difference in SWR is observed at 5% FAC between matrix modified composite and r-PET/FAC composite.

The reduction in SWR could be owing to the improvement in the toughness or fracture strain of the matrix. Neat r-PET displayed fine wear surface showing brittle nature of the plastic (Figure 3.22A). The river structure (Lothar et al,1981) displayed by the wear surface of r-PET blend (Figure 3.22B) provides the evidence for reduction in wear rate. Large number of dangling units in M-r-PET/FAC composite, shown in the SEM micrograph (Figure 3.22C) could be due to tearing resistance of the material before fracture. However, for composites with FAC greater than 5%, loss of particles as explained earlier could be lead to loss of material that increases the wear rate.
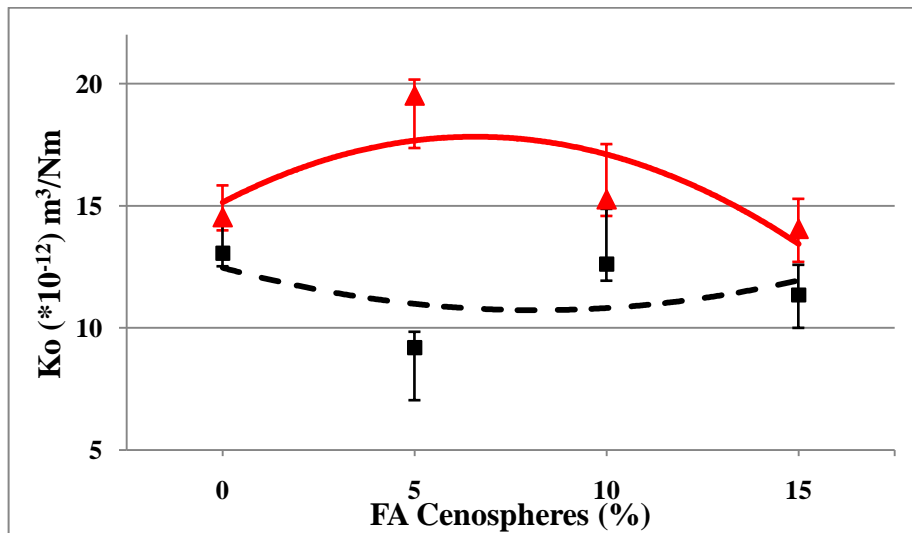
Figure 3.21: Effect of r-LDPE on the wear property of r-PET and its composites.

Although the matrix is made flexible by blending it with r-LDPE, the problem of de-bonding of FAC remains unresolved. The SEM pictures shown in Figure 3.23 provide sufficient evidence for de-bonding of FAC from the r-PET matrix both in Flexural and wear samples. Figure 3.33A displays de-bonded sites in flexural samples where as Figure

3.23B shows de-bonded sites filled with wear debris. In order to improve wetting, FAC is surface treated before introduction into matrix

3.5 RESULTS OF TESTING R-PET/ T-FAC COMPOSITES FOR FLEXURAL AND WEAR PROPERTIES

Treatment of FAC is envisaged to improve the interface between the matrix and the reinforcement. FAC are chemically treated with (3-aminopropyl) trimethoxy silane (3APTMS), as elaborated in section 2.2.7, and the coated FAC are tested for coating through FTIR spectroscopy. Figure 3.24 is a spectrograms for FAC treated with 10% 3APTMS. The spectrograms displays Amine peak in the wavelength range of 3300 cm^{-1} to 3500 cm^{-1} and C-H stretch in the wavelength range from 2900 cm^{-1} to 3000 cm^{-1} which are the characteristics of 3APTMS. Further the results of FTIR spectroscopy are cross verified by TGA analysis. The presence of these chemical grous is helpful in binding FAC to r-PET.

A. Neat r-PET   B. M-r-PET
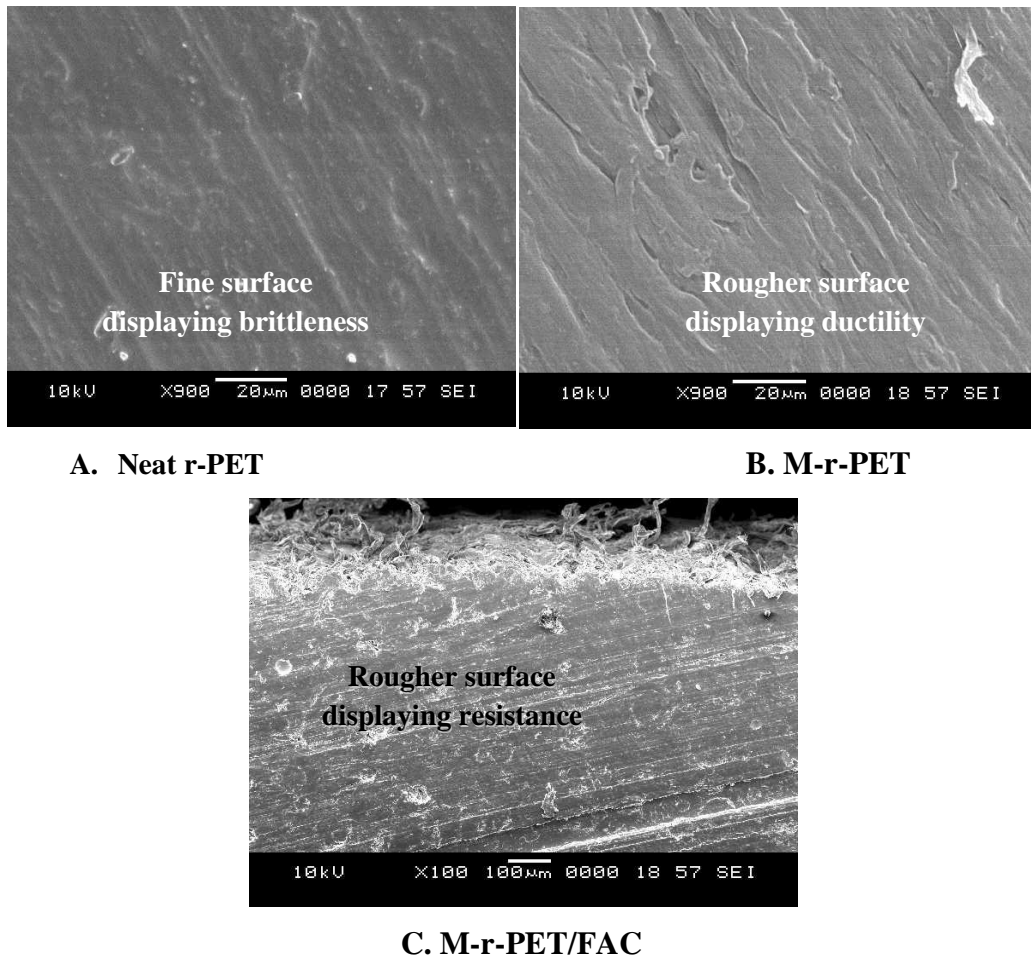
C. M-r-PET/FAC

Figure 3.22: Micrographs of wear surfaces of matrix modified composites
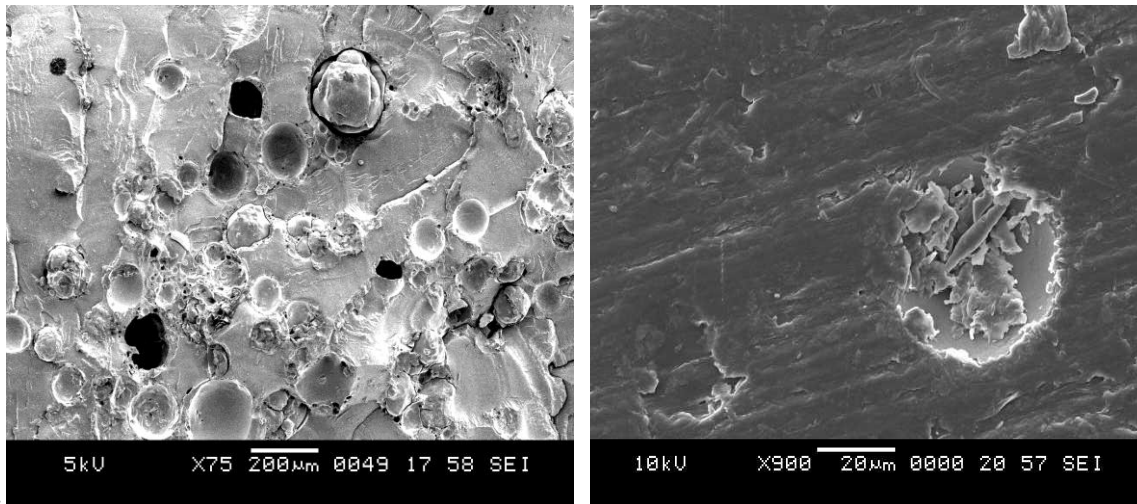
A. Fracture surface of r-PET/FAC   **B. Wear surface of M-r-PET/FAC**

Figure 3.23: SEM pictures showing debonding of FAC from the matrix.
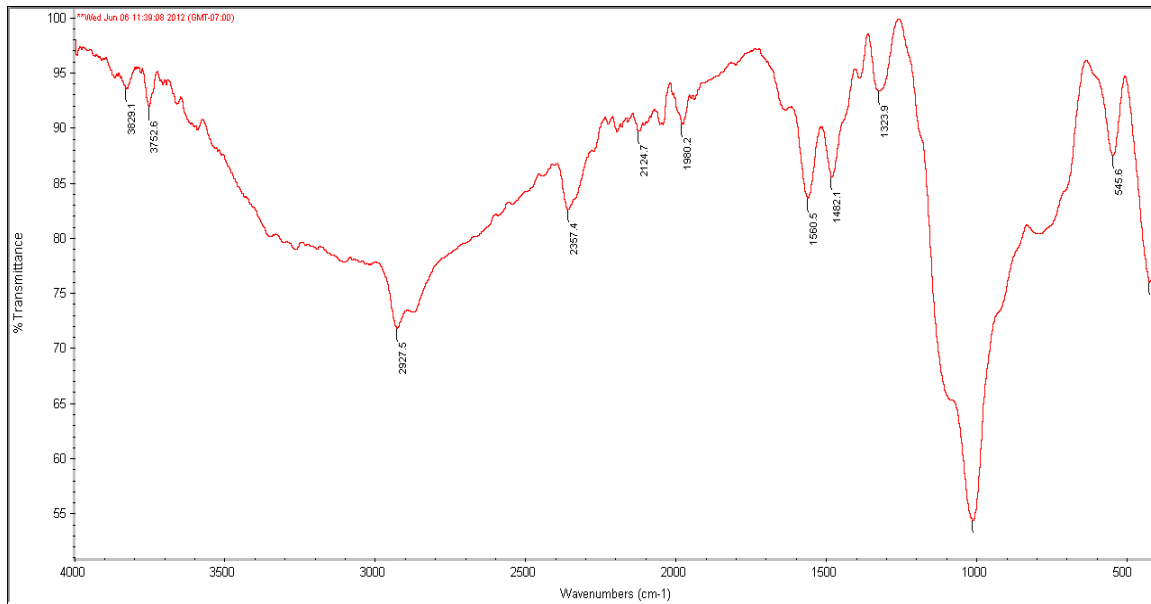
Figure 3.24: FTIR spectrogram showing presence of Silane coating on FAC treated with 10% 3APTMS.

The results of flexural (Sections 3.5.1) and wear tests (Sections 3.5.1) conducted on the samples of r-PET matrix, reinforced with treated FAC are provided in the following sections.

3.5.1 Flexural properties of r-PET/T-FAC composites

In this section, effects of surface treating FAC on Flexural strength, fracture strain, modulus and toughness are shown in the Figure 3.25. The analysis of data pinpoints that T-FAC reinforced r-PET display appreciable improvement in flexural strength and modulus. Fracture strain and toughness, however, drops marginally.. The improvement in the properties could be the result of binding of T-FAC to the matrix. The SEM picture, shown Figure 3.26, is for 10% 3APTMS treated FAC composite. This picture shows improvement in binding between FAC and matrix when compared to the untreated FAC composite (Figure 3.10).

A Flexural Strength

B. Fracture Strain

C. Toughness

D. Elastic Modulus
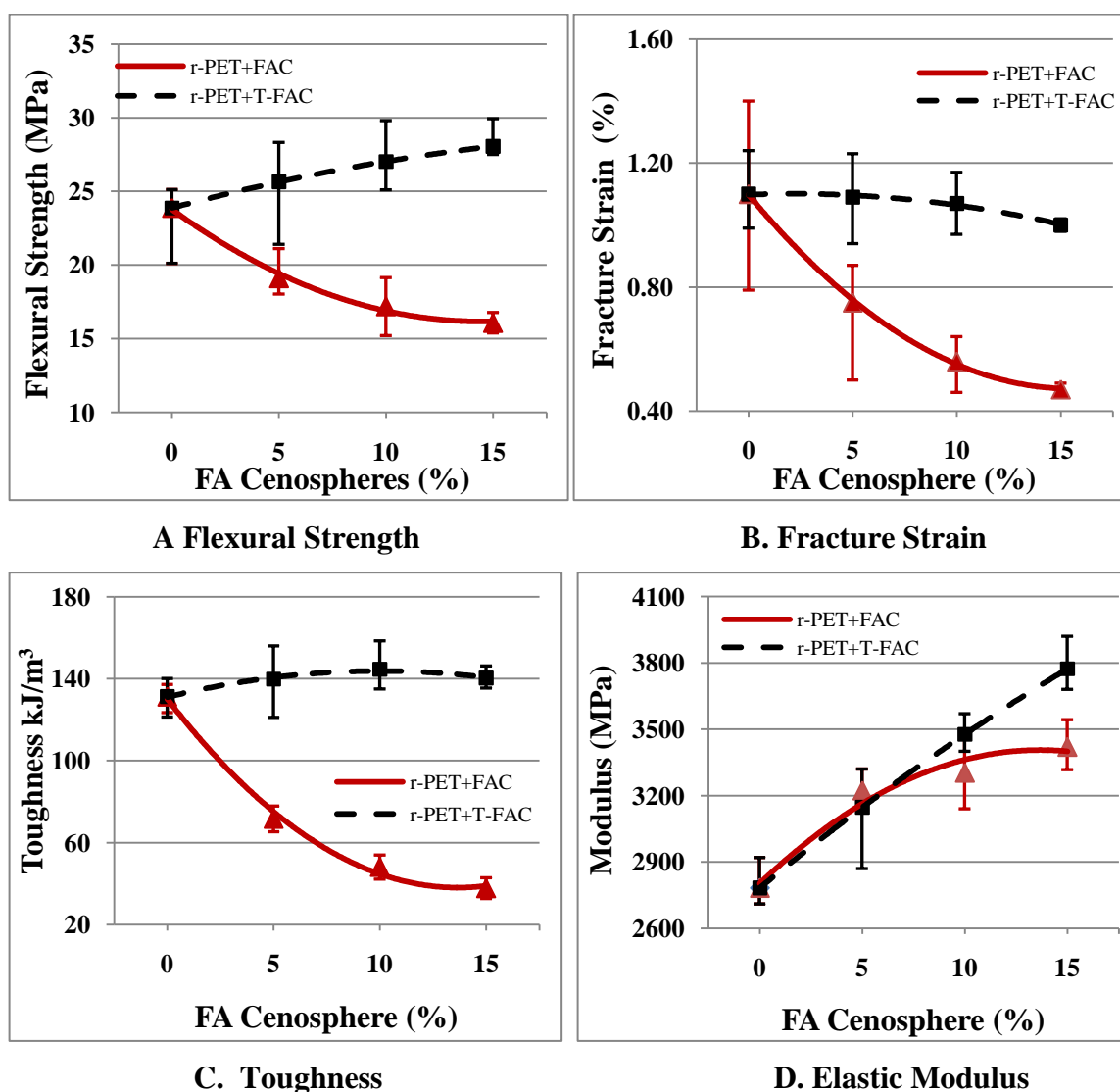
Figure 3.25: Flexural properties of r-PET/T-FAC
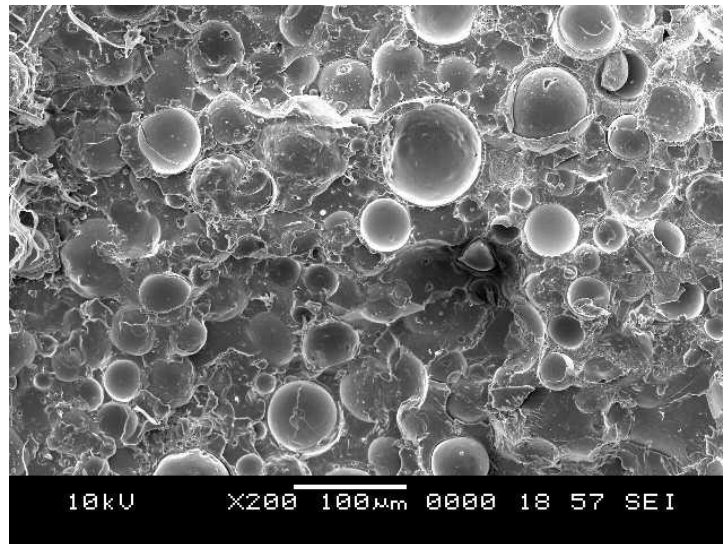
Figure 3.26: SEM micrograph of fracture surface showing binding between T-FAC and r-PET matrix

The results presented in this section indicate that the objectives to improve strength by properly binding the FAC to r-PET matrix can be met by treating it with 3APTMS. The evidence for improved binding is provided in the SEM micrograph. The loss in the strength of the composite due to matrix modifications can be recovered through surface treatment of the FAC.

3.5.2 Wear properties of r-PET/T-FAC composites

Figure 3.27 compares the wear properties of r-PET/FAC composite with that of r-PET/T-FAC composite. The former composite display a initial hike in the wear rate which subsequently reduces on increasing the FAC content. The initial increase in the wear rate is due to the weakening of the composite due to debonding of FAC leading to loss of strength. The improvement in the wear rate at higher content of FAC may be owing to the properties of T-FAC particles. Surface treated FAC composite display an improvement in the wear rate at lower contents. This could be due to improvement in binding of the filler to the matrix. A marginal raise in the wear rate of surface treated FAC composite can be due to the brittleness of the matrix. It is to be noted that, although there is raise in the wear rate of surface treated FAC composite, the rate of wear remains lower when compared to r-PET/FAC composite.
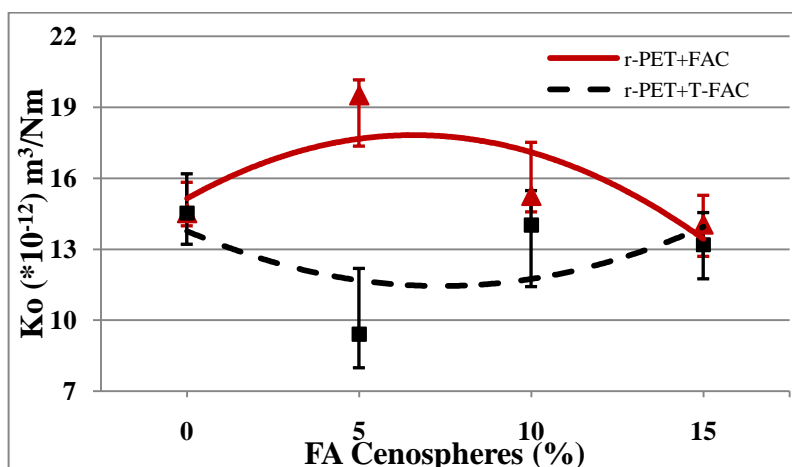
Figure 3.27: Wear properties of r-PET/T-FAC composite in comparison to r-PET/FAC composite

Modification of r-PET both in terms of matrix and reinforcement (M-r-PET/T-FAC) is tried in the next stage of this work. Results of the study on the flexural properties of M-r-PET/T-FAC composites are presented in the Section 3.6.1.

3.6 RESULTS OF MATRIX BLENDING AND TREATING REINFORCEMENT

Composites with blended matrix (30% r-LDPE) reinforced with treated FAC (10% 3APTMS) are studied at this stage for flexural and wear properties.
.

3.6.1 Flexural properties of M-r-PET/T-FAC composites

In this section, results on the effect of both matrix and reinforcement modifications is put forward. This study is a prerequisite to perform optimization procedures on M-r-PET/T-FAC composite through Taguchi method. The properties of M-r-PET/T-FAC in comparison to r-PET/FAC are given in the Table 3.28. The results portray the effect of matrix modifications and the surface treatment of FAC on the flexural properties of r-PET composite. Figure 3.28 display comparative results for the r-PET/FAC and M-r-PET/ T-FAC composite. The M-r-PET/T-FAC composite shows improvements in the flexural strength (Figure 3.28.A), fracture strain (Figure 3.28.B) and the toughness (Figure 3.28.C). The observed results could be the result of improved flexibility of the matrix and at the same time well bound reinforcement. The decrease in the modulus of M-r-PET/T-FAC composite is evident from the Figure 3.28.D. Except the modulus all other properties are declining for r-PET/FAC composite. The experiments performed on matrix modifications (Section 3.4.1) and surface modifications of reinforcements

(Section 3.5.1) indicate that the matrix modifications carried out with r-LDPE improves the fracture strain. This is due to the properties of the materials used for blending. The surface modification of FAC improves the flexural strength of the composite. Surface treated FAC binds well with the matrix leading to better transfer of loads. The SEM picture shown in the Figure 3.29 display better bound T-FAC and plasticity in the matrix. Effectively these modifications toughen the r-PET composite that makes it suitable for engineering applications like composite gears. Moreover, the modulus requirement of a material for engineering applications is well maintained by the composite, especially in the modified form.

A. Flexural Strength

B. Fracture Strain

C. Toughness

D. Elastic Modulus
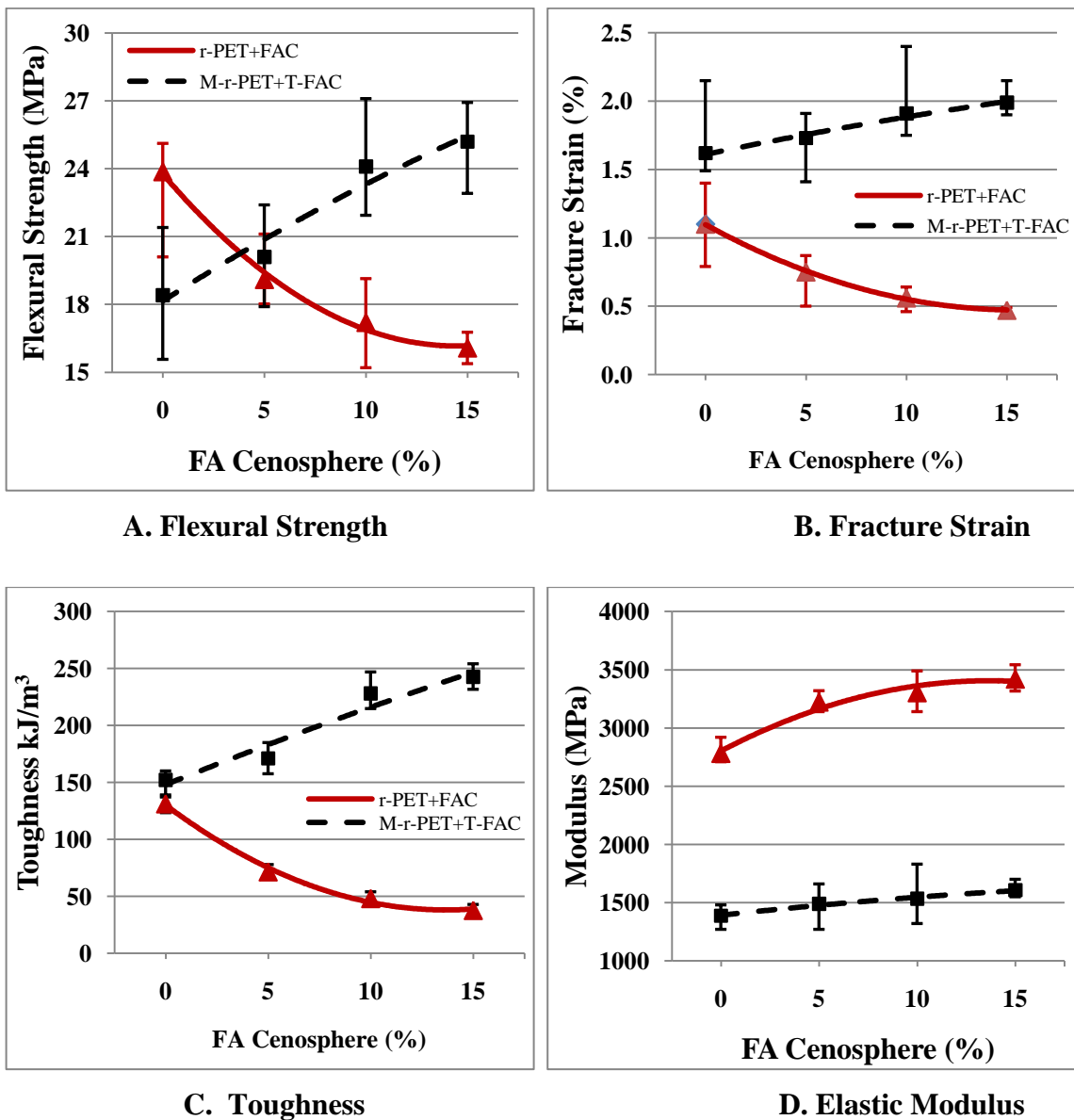
Figure 3.28: Flexural properties of M-r-PET/T-FAC composites

It is to be noted that in all these experiments the matrix and reinforcements are treated and studied for a single level of the component. The matrix is modified with 30% r-LDPE for the study of its effect on r-PET/FAC composite. Similarly FAC is treated with 10% 3APTM silane and its effect on blended r-PET composite is studied. However, to optimize the moulding and material parameters the study must be carried preferably at more than two levels. The results of this work are presented in section 3.7.
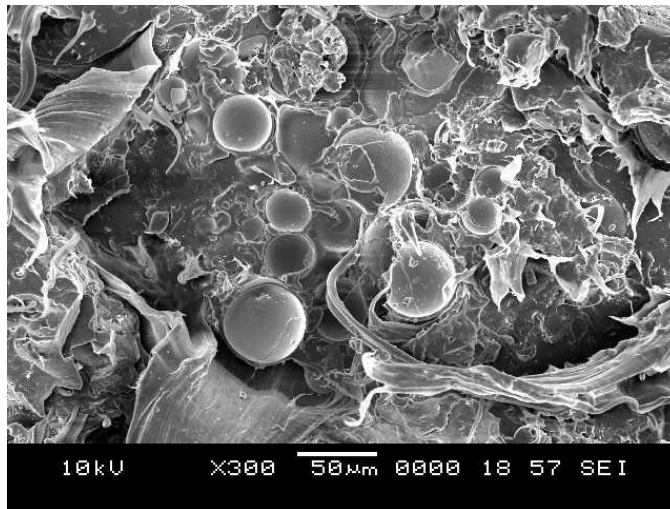
Figure 3.29 Fracture surface of M-r-PET/T-FAC composite showing plasticity in the matrix and well bound T-FAC

3.6.2 Wear properties of M-r-PET/T-FAC composites

The results of wear properties of matrix modified and surface treated FAC filled r-PET composite is presented in the Figure 3. 30. The Figure clearly shows an improvement in the wear property of the M-r-PET/T-FAC composite owing to surface treatment of FAC in matrix modified r-PET composite. However SWR increases on reinforcing the composite above 10% of T-FAC. The results on wear properties presented upto this section bring out the facts that extent of matrix modification and surface treatment plays key role in deciding the wear property of the composite. However, for a minimum SWR, optimization of material and process parameters is very essential. Generally, the samples are made at a definite level of operating parameters. Optimizing these operating parameters along with the material parameters can lead to a combination that may prove

to be beneficial to the performance of the composite. Results of optimization of material and process parameters are provided in the next section.
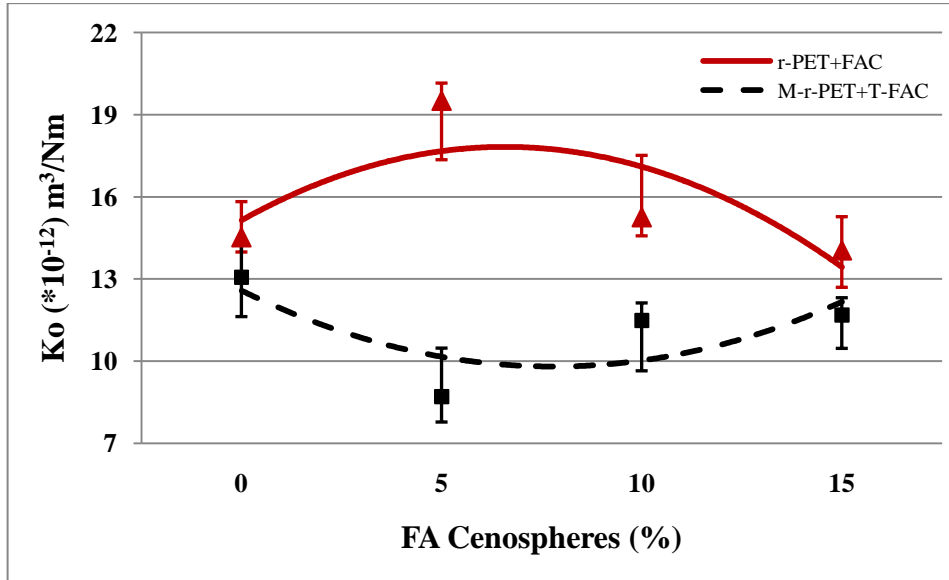
Figure 3.30: Wear properties of M-r-PET/T-FAC composite in comparison to r-PET/FAC composite

3.7 RESULTS OF OPTIMIZING PROCESS AND MATERIAL PARAMETERS FOR M-R-PET/T-FAC COMPOSITES

The results of r-PET/FAC composite studied using Taguchi's DOE approach are presented in the Section 3.2. Five parameters are considered in the study and it is observed that only three parameters are significant for all the responses. These three parameters are moulding temperature, moulding time and FAC content. Moulding time and mould cooling types are less significant. The study on the matrix modification presented in the section 3.4.1, reveals that r-LDPE blended r-PET show improvement in flexibility by reducing modulus of the composite. The surface modifications given to FAC by 3APTM Silane (Section 3.5) improves both flexural and wear properties of the composite. The matrix and the reinforcement studies carried in previous section seem to have limited scope as the matrix is blended with a constant 30% r-LDPE in the composite. Similarly, the effect of 3APTMS is studied at 10% concentration. These studies across different levels of the variables demand full factorial experiments. However, this is a tiresome and time consuming task as it demands the need to perform

huge number of experiments. Hence, at this stage Taguchi's DOE is applied to study the effect of moulding and material parameters on the responses. The three significant moulding parameters (CTQ) observed in section 3.2.1, viz. moulding temperature, moulding time and FAC content in the composite are chosen. The other two are wt % of r-LDPE and wt % of 3APTMS. All these five parameters are studied at three levels as described in that section. The results of experimentation conducted using L_{27} OA is presented in the following sections.

3.7.1 Optimization of flexural properties of M-r-PET/T-FAC composites

M-r-PET/T-FAC is studied to optimize compression moulding for recycling r-PET. Similar to previous DOE study, five parameters are considered at three levels with L_{27} OA for the experimentation. The responses considered for the study of flexural properties are flexural strength, fracture strain, toughness and modulus. The results obtained are tabulated in the Table 3.14. Ratio of mean to variance (S/N) function used for further analysis are tabulated in the Table 3.15

3.7.2 Analysis of mean S/N ratios of flexural properties

The average values of S/N ratios for each factor at level 1 to level 3, used to decide the optimum parameter of flexural strength is shown in Table 3.16.

Table 3.14: Flexural and wear properties of M-r-PET/T-FAC composites

Expt No.	Mean flexural strength (MPa)	Mean fracture strain (%)	Mean toughness (kJ/m^3)	Mean flexural modulus (MPa)	SWR (*10^{-12}) (m^3/Nm)
1	16.43	1.05	172.23	1315	5.09804
2	17.68	1.02	170.81	1356	2.36451
3	18.09	1.12	187.33	1652	3.53514
4	18.71	0.85	165.27	1452	0.67087
5	26.34	1.02	220.44	1802	0.43853
6	13.41	1.26	164.29	1362	1.36137
7	22.71	0.84	194.10	3421	0.42417
8	12.26	1.09	152.90	1358	0.98177
9	22.03	1.17	215.42	1443	0.92627

10	21.99	1.11	196.77	3565	1.53115
11	11.56	1.35	153.31	1353	0.81574
12	20.49	1.58	237.16	1493	0.34148
13	17.30	1.09	163.95	1494	0.97628
14	23.16	1.47	266.91	3264	1.94832
15	28.90	1.23	252.67	3256	0.53430
16	19.39	1.12	183.31	2221	0.92988
17	23.18	1.17	210.06	3149	5.12480
18	12.22	2.10	203.31	1413	0.23240
19	23.39	0.99	179.62	2395	9.57727
20	32.26	1.04	231.76	2342	0.88201
21	21.21	1.37	209.38	1780	0.80461
22	28.31	1.01	206.67	2621	1.03275
23	16.42	1.76	208.46	2360	0.81283
24	19.51	1.67	226.87	2103	6.57591
25	17.75	1.36	184.53	1820	0.70916
26	17.56	1.77	210.49	3002	6.25508
27	21.05	1.49	221.13	2920	1.11944

Table 3.15: Mean S/N ratios calculated for the flexural and wear properties of M-r-PET/T-FAC composites

Expt. No.	S/N ratio (flexural strength)	S/N ratio (fracture strain)	S/N ratio (toughness)	S/N ratio (flexural modulus)	S/N ratio (SWR)
1	24.31	0.42	104.72	62.38	225.852
2	24.95	0.17	104.65	62.65	232.525
3	25.15	0.98	105.45	64.36	229.032
4	25.44	-1.41	104.36	63.24	243.467
5	28.41	0.17	106.87	65.12	247.160
6	22.55	2.01	104.31	62.68	237.320
7	27.12	-1.51	105.76	70.68	247.449
8	21.77	0.75	103.69	62.66	240.160

9	26.86	1.36	106.67	63.19	240.665
10	26.84	0.91	105.88	71.04	236.300
11	21.26	2.61	103.71	62.63	241.769
12	26.23	3.97	107.50	63.48	249.333
13	24.76	0.75	104.29	63.49	240.209
14	27.29	3.35	108.53	70.28	234.207
15	29.22	1.80	108.05	70.25	245.444
16	25.75	0.98	105.26	66.93	240.631
17	27.30	1.36	106.45	69.96	225.806
18	21.74	6.44	106.16	63.00	252.675
19	27.38	-0.09	105.09	67.59	220.375
20	30.17	0.34	107.30	67.39	241.091
21	26.53	2.73	106.42	65.01	241.888
22	29.04	0.09	106.31	68.37	239.720
23	24.31	4.91	106.38	67.46	241.800
24	25.81	4.45	107.12	66.46	223.641
25	24.98	2.67	105.32	65.20	242.985
26	24.89	4.96	106.46	69.55	224.075
27	26.47	3.46	106.89	69.31	239.020

Table 3.16: Response table for the flexural strength of M-r-PET/T-FAC composite

Level	Pressure (MPa)	3APTMS (%)	r-LDPE (%)	Temperature (˚C)	FA Cenosphere (%)
1	25.17	25.87	26.18	25.95	23.58
2	25.60	26.31	25.60	26.07	26.07
3	26.62	25.21	25.62	25.17	27.75
Delta	1.45	1.1	0.59	1.10	4.17
Rank	2	3	5	4	1
Significance	Very Significant	Significant	Less Significant	Significant	Very Significant

From the response table, it is observed that the FAC content in the composite is the most critical factor followed by moulding pressure, silane coating and moulding temperature. R-LDPE content however is of less significant. The main effects diagram for flexural strength is shown in the Figure 3.31.
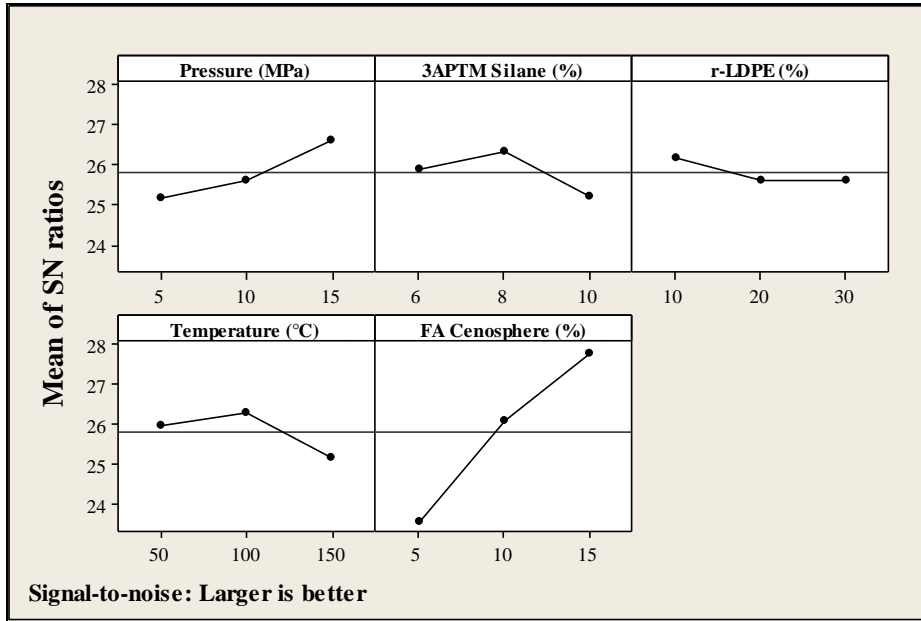
Figure 3.31: Main effects diagram of flexural strength for M-r-PET/T-FAC.

By comparing the main effects diagrams of r-PET/FAC (Figure 3.5) and M-r-PET/T-FAC composite (Figure 3.31) one can note that, FAC content is the most significant factor in both the cases however, the gradient in the M-r-PET/T-FAC case is upward. The reversal of gradient can be attributed to the treated FAC bound well with the matrix. Although 3APTMS is at third rank it amplifies the effects of FAC on the flexural strength of r-PET by reversing its gradient. A drop in S/N for 10% APTMS can also be observed in the Figure. Further, the increase in delta due to FAC is 2.5, when the filler is raised from 5 to 10% in the composite and is 1.7 for the next 5% rise. These observations could be due to agglomeration of T-FAC in the composite. 15 % of FAC at higher (10%) 3APTMS concentration may increase the chances of electro static attraction between the FAC particles and get agglomerated. The SEM picture in Figure 3.32 shows such regions of agglomeration in r-PET composite sample at 15% of T-FAC. The deficiency of matrix in the agglomerated region locally reduces the strength of the composite. The

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weak bonding between T-FAC particles provide an easy path for the moving crack leading to failure.

Moulding pressure is second most CTQ parameter. As explained earlier, increase in the moulding pressure lead to reduction in the density of pores formed in the sample during compression moulding. A pore being a source of surface energy for a growing crack accelerates its growth. Lower pore density in a composite sample improves flexural strength.
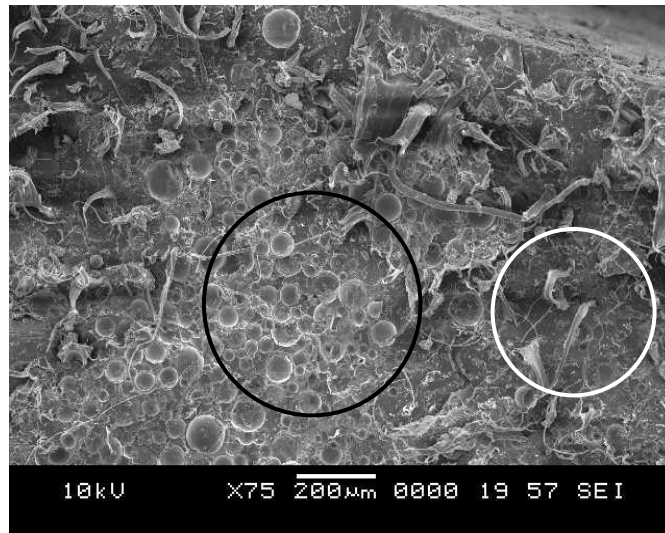
Figure 3.32: r-PET/30% r-LDPE/15% FAC (10% APTMS) composite showing regions of agglomeration of fillers

R-LDPE displays a downward trend and the decrease in S/N for flexural strength is marginal (Significance rank 5). This is in accordance to the results perceived as explained in the section on matrix modifications. When blended with each other r-LDPE being a rubbery plastic reduces the strength of r-PET, which is a stiffer plastic. However, as observed earlier the drop in the strength with r-LDPE is lower when compared to other plastics used in the blending experiments. A low rank for r-LDPE is thus justified.

Table 3.17 is the response table for fracture strain. The analysis of S/N ratio for fracture strain discloses that matrix modification of r-PET with r-LDPE is a most significant factor. Significant raise in delta with an increase in r-LDPE from 5 to 15% can be clearly

noted from the table. Moulding pressure and FAC content are at second and third positions. Silane coating and moulding temperature are less significant factors. FAC being ceramic by nature yields very less and hence it has a limited effect on the fracture strain of the composite. It offers higher strength to the composite by sharing the load but less deformable. However, r-LDPE being rubbery can improve yielding of the composite, which can clearly be seen in the main effect graphs for fracture strain (Figure 3.33).

Table 3.17: Response table for fracture strain in terms of mean S/N ratio

Level	Pressure (MPa)	3APTMS (%)	r-LDPE (%)	Temperature (°C)	FA Cenosphere (%)
1	0.33	1.34	0.31	1.71	2.59
2	2.46	1.79	2.07	1.61	1.97
3	2.61	2.28	3.02	20.9	0.84
Delta	2.29	0.94	2.71	0.47	1.74
Rank	2	4	1	5	3
Significance	Very Significant	Less Significant	Very Significant	Less Significant	Significant

From the main effect diagram shown in the Figure 3.33, it can be seen that r-LDPE shows a positive slope indicating a better strain at higher concentrations. However, FAC has a negative gradient suggesting lower concentration in the composite for better strain. The slopes for pressure and 3APTMS are also positive. Thus, from Figure 3.33 the optimal parametric levels for fracture strain could be A3, B3, C3, D2 and C1.

A collective effect of matrix and reinforcement modifications is studied by analyzing S/N ratio for toughness. The response table and the main effect graphs are given in the Table 3.18 and Figure 3.34 respectively. FAC, r-LDPE content and moulding pressure are the three high ranked parameters. Reinforcement with T-FAC strengthens the composite where as blending it with r-LDPE improves yielding. The collective effect is visualized in terms of increment in the energy absorbed while deforming the composite.

The main effects diagram shows an upward gradient for all the three significant factors with optimum levels being A3, C3 and E3. 15% of T-FAC content provides highest toughness to the composite. However, the raise in S/N slows down above 10% it may be due to the agglomeration of the FAC particles at higher concentrations. Intermediate (B2-8%) level of coating is optimum. Further, higher pressures compress the charge better, decreasing the void density. These factors could improve the toughness.
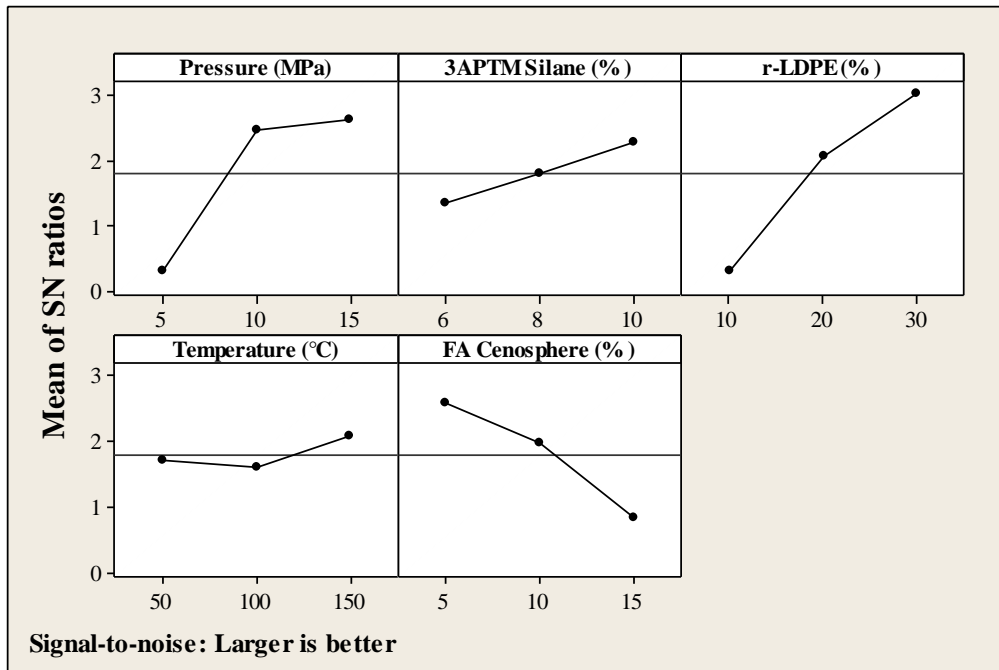
Figure 3.33: Main effects diagram of fracture strain for M-r-PET/T-FAC.

Table 3.18: Response table for toughness in terms of mean S/N ratio

Level	Pressure (MPa)	3APTMS (%)	r-LDPE (%)	Temperature (°C)	FA Cenosphere (%)
1	105.2	105.6	105.2	106.1	105.0
2	106.2	106.2	106.0	106.0	106.2
3	106.4	105.9	106.5	105.7	106.6
Delta	1.2	0.6	1.3	0.4	1.5
Rank	3	4	2	5	1
Significance	Very Significant	Less Significant	Very Significant	Less Significant	Very Significant
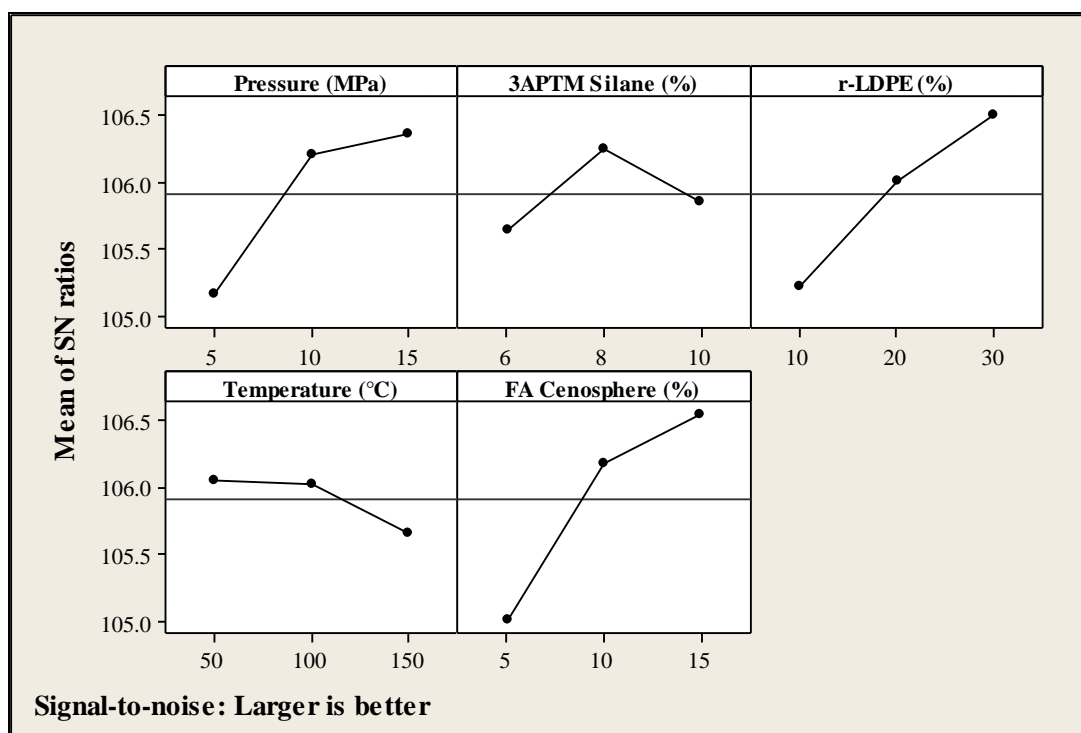
Figure 3.34: Main effects in terms of S/N ratio for toughness

The response table for elastic modulus is tabulated in the Table 3.19. T-FAC and moulding pressure are very significant for modulus. Figure 3.35 display the main effects in terms of S/N ratio for modulus. Moulding pressure, T-FAC content and silane coupling show a positive gradient. The optimum levels are A3, B3 and F3. FAC being hard ceramic filler improves the modulus of the composite. Reduction in the void volume resulted due to moulding pressure that acts positively towards elastic modulus. Reinforcement treatment is positive on modulus. Further, the treatment leads to an increment in the ranking of FAC from three to one, making it most significant parameter to the modulus. The matrix modification however has a negative gradient on the modulus with optimum level at C1. Rubbery nature of the plastic may be the reason for the observed effect.

3.7.3   Optimization of wear properties of M-r-PET/T-FAC composites

The samples prepared in accordance with the L_{27} OA, explained in section 2.2.6, are tested for wear properties of M-r-PET/T-FAC composite. The mean values of SWR is tabulated in the Table 3.14 and corresponding S/N (Lower is better) is in the Table 3.15.

Table 3.19: Response table for toughness in terms of mean S/N ratio

Level	Pressure (MPa)	3APTMS (%)	r-LDPE (%)	Temperature (°C)	FA Cenosphere (%)
1	64.11	65.17	66.55	65.94	63.83
2	66.78	66.37	66.41	66.44	65.93
3	67.37	66.73	65.30	65.87	68.50
Delta	3.26	1.55	1.24	0.57	4.66
Rank	2	3	4	5	1
Significance	Very Significant	Significant	Significant	Less Significant	Very Significant
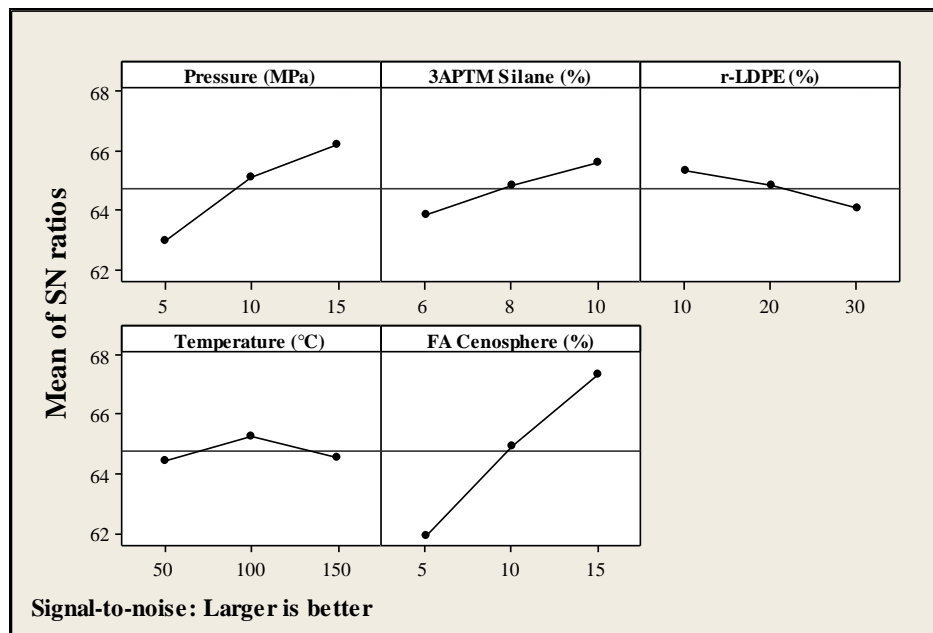
Figure 3.35: Main effects diagram for modulus (M-r-PET/T-FAC)

3.7.4 Analysis of mean S/N ratios of SWR

The significance of individual parameters on the wear rate of r-PET composite and their optimum levels, in terms of their S/N ratios are illustrated in Table 3.20.

Table 3.20: Mean value of S/N ratio for SWR of M-r-PET/T-FAC.

Level	A	B	C	D	E	F	G	H	I
1	238.2	235.4	234.6	224.8	237.4	241.2	221.0	238.6	240.5
2	240.7	239.2	240.2	238.9	236.5	237.9	241.2	239.0	234.3
3	235.0	239.3	239.1	240.1	239.9	234.7	241.6	236.3	239.0
Delta	5.8	3.9	5.5	5.3	3.4	6.6	10.6	2.7	6.2
Rank	4	7	5	6	8	2	1	9	3
Optimum Level	15	6	1	150	20	600	220	150	10

From the response table (Table 3.20), the optimum levels of moulding and material parameters for M-r-PET/T-FAC composite are found to be moulding pressure (A3), 3APTM Silane (B1), r-LDPE (E2), moulding temperature (H3), and weight fraction of FAC (I2). Similarly the optimum levels of wear parameters are Load on specimen (C1), sliding distance (D1), speed of rotation (F3) and surface roughness (G1) which is similar to that for r-PT/FAC composite. An insight in to the results of experimentation points to the facts that FAC content and the moulding pressure takes third and fourth places respectively. This is in contrast to the observations with r-PET/FAC composite where the wear parameters are very prominent taking 1 to 4 significant ranking. Although there were changes in the significant ranks of wear parameters, their optimum levels remain unaltered.

The main effect diagram for moulding and material parameters for M-r-PET/T-FAC composite is shown in the Figure 3.36. In contrast to r-PET/FAC composite (Figure 3.11) the modified composite display optimum SWR at intermediate levels of FAC. The localized accumulation of T-FAC at 15% level leads to increase in SWR owing to less availability of matrix for resisting frictional losses. The optimum level of r-LDPE is also intermediate (20%). Addition of r-LDPE to the matrix makes it more flexible. Under friction, r-LDPE deforms the matrix elastically and resists the loss of matrix. However at higher concentrations (30%), loss in the strength leads to increase in material losses. The optimum level for 3APTMS is 6%. At higher concentrations, the ability of T-FAC for accumulation leading to agglomeration increases. At higher temperatures and pressures,

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the charge of the composite can flow better reducing the bulk volume of voids and hence SWR, as explained earlier. The data collected on the flexural and wear properties of M-r-PET/T-FAC composite and the results of experimentation are used to optimize material and process parameters of compression moulding. Six Sigma DMAIC optimization techniques are utilized to achieve the goal. Systematic adaptation of these techniques is explained in the following section.
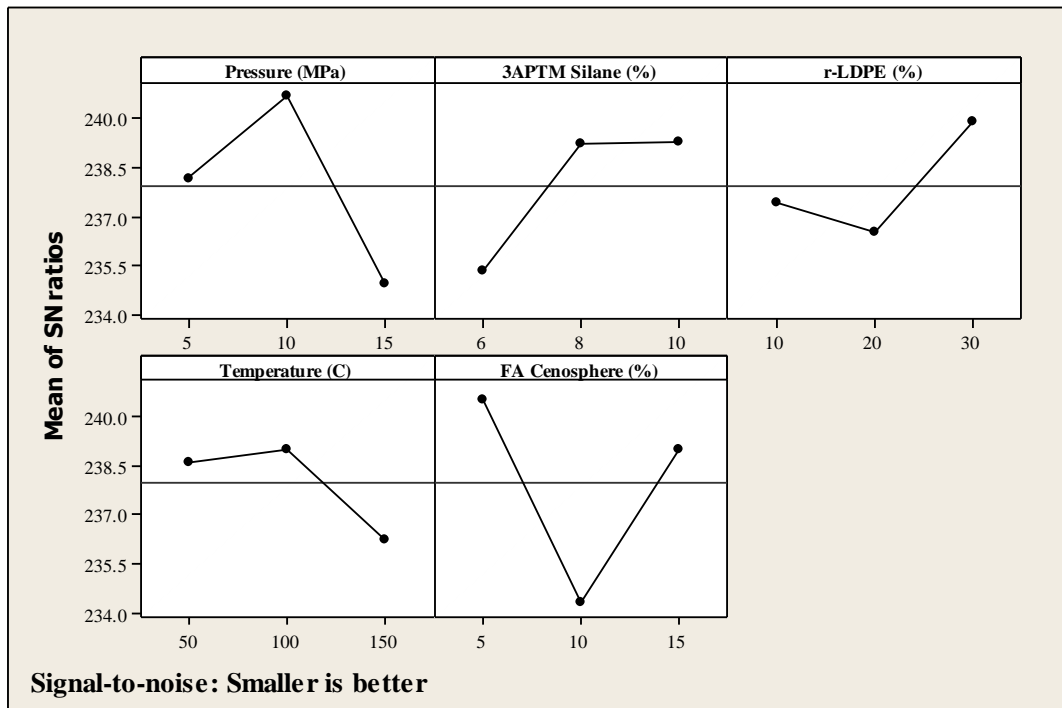
Figure 3.36: Main effects diagram of moulding and material parameters for SWR (M-r-PET/T-FAC)

3.7.5 Discussion on the results of flexural and wear properties of M-r-PET/T-FAC Composites

Matrix of a PMC transfers load to the reinforcement on straining. M-r-PET being blended with r-LDPE, is better strainable and finds it easier to transfer the load. T-FAC being well bound to the matrix absorbs load through the interface and hence provides better strength to the composite. A sample of M-r-PET/T-FAC composite has stiff r-PET macromolecule impregnated with T-FAC and entangled coil of r-LDPE impregnated with T-FAC as shown in the Figure 3.37. During fracture, a crack growing transverse to r-PET chain is

resisted by the covalent bonds of the polymer back bone. On the other hand the crack, propagating in the longitudinal direction (Figure 3.38) grows by breaking hydrogen bonds that binds neighboring polymer chains. Presence of hard T-FAC in the path of the crack resists such a growth by stopping it at the surface or by moving it away by changing direction of the crack. Such a resistance to the propagating crack improves strength and energy absorbed during fracture of the composite.

In the case of r-LDPE impregnated with T-FAC, the rupture of the composite is postponed by r-LDPE by straining extensively. Further, a straining chain of the polymer grips itself to T-FAC flexurally (Figure 3.38). The visco-elastic behaviour of r-LDPE enhances the possibility of such gripping and improves the load sharing between them. A mechanism of this type will not only improve strainability of the composite but also may improve its strength and toughness, as noted in the preliminary studies during material development. The movement of a crack reaching such a system could be withheld by r-LDPE, supported by T-FAC, till the polymer chain ruptures. Later the movement of the crack is resisted by T-FAC.

Comparison between the wear parameters of r-PET/FAC and M-r-PET/T-FAC (Figure 3.27) composites bring out the facts that mean SWR improves maximum by 42% owing to material modifications. The reduction in material loss could be due to the improved plasticity of the matrix. The dislodging of lump of the matrix is delayed by stretching of r-LDPE from the sample is retained with itself till it ruptures as shown in the Figure 3.39. Such a delay in the material loss improves wear resistance of the composite. Further, well bound T-FAC, impregnated in r-LDPE, provides additional strength and support to the deforming matrix. Plastic stretching and improved binding of T-FAC is confirmed by the SEM micrographs shown in Figures 3.40.

Moulding/material parameters for r-PET/FAC (Table 3.13) were less significant than wear parameters as they took ranking lower than 4. However in case of M-r-PET/T-FAC (Table 3.20) composites, FAC content and moulding pressures take third and fourth ranking respectively. Although optimal level for pressure is 15 MPa for both composites, FAC content is optimum at intermediate level (10%) unlike that for r-PET/FAC which is 15%.
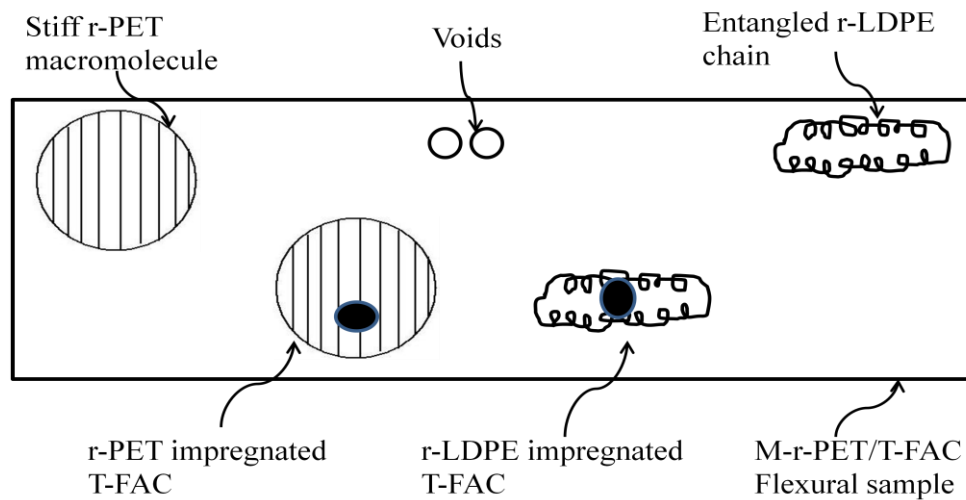
Figure 3.37: Components of M-r-PET/T-FAC composite
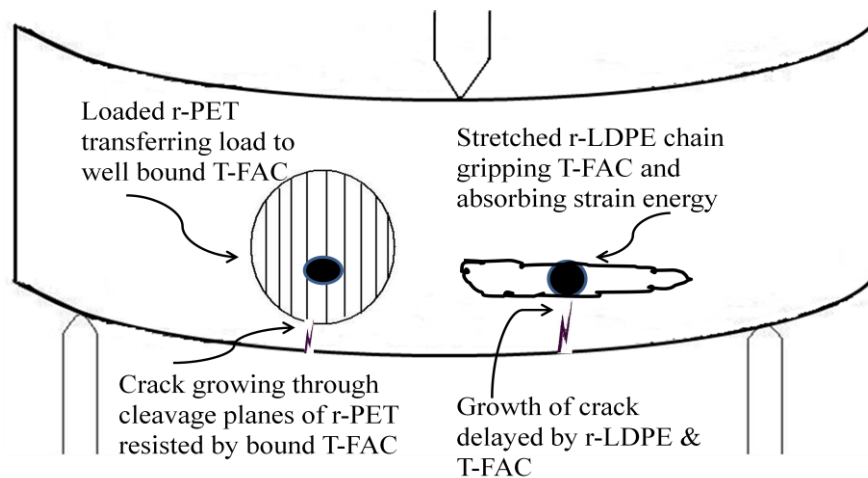
Figure 3.38: Proposed mode of fracture for M-r-PET/ T-FAC composite.

Further, the optimum level for 3APTMS is 6%, which is the lowest level in the experimentation. Increasing T-FAC beyond 10% could lead to agglomeration of the particles leading to deficiency of matrix locally. Further, higher concentrations of 3APTMS increase the density of static charges on the surface of FAC. Denser charges on the surface increases probability of mutual attraction leading to agglomeration. Such a situation eases loss of reinforcement under friction.
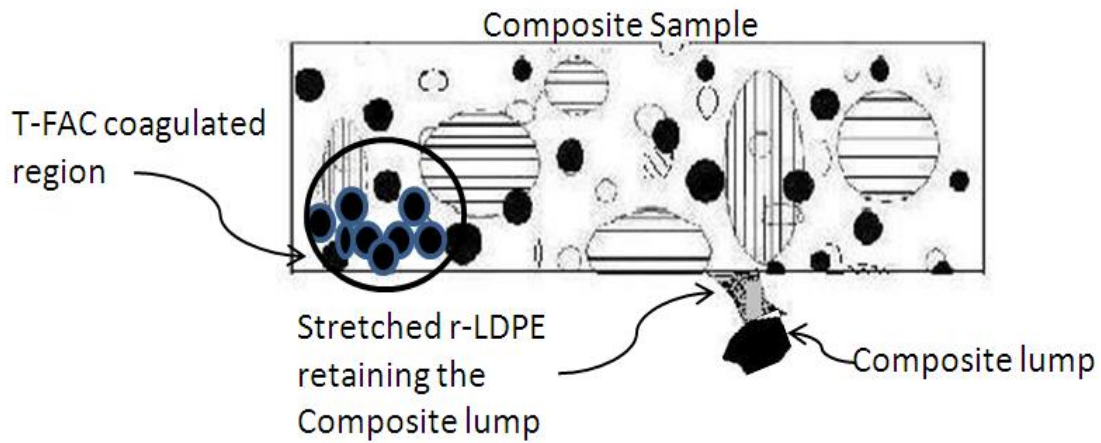
Figure 3.39: Proposed mode of wear loss in M-r-PET/ T-FAC composite
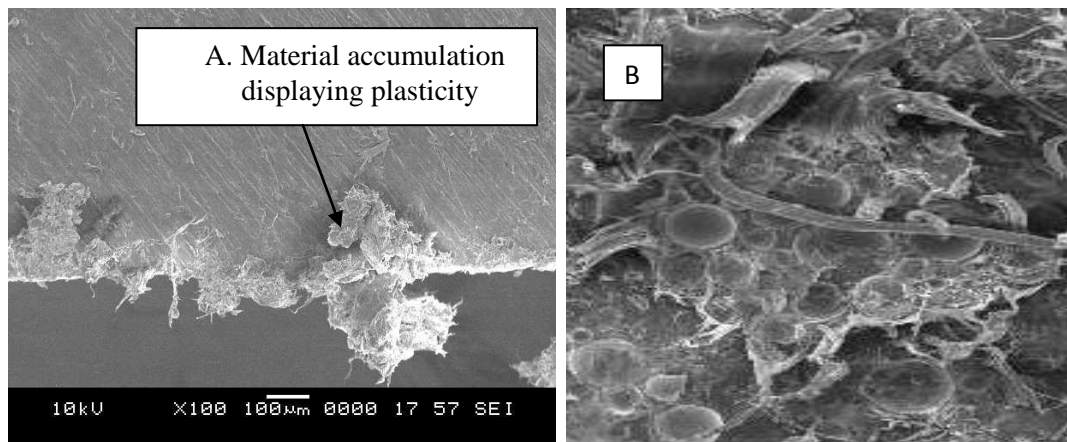
Figure 3.40: Wear surface displaying stretching of matrix(A) and fracture surface displaying agglomeration of T-FAC in M-r-PET/ T-FAC composite (B)

3.8 SIX SIGMA DMAIC OPTIMIZATION OF THE MATERIAL AND PROCESS DEVELOPED FOR TOUGHNESS AND SWR

DMAIC (Define, Measure, Analyze, Improve and Control) approach, a systematic method suggested is applied to optimize compression moulding process for r-PET.

3.8.1 Define

The issues related to r-PET/FAC composite are brittleness and poor binding of reinforcements. These problems prevent recycling these materials for their engineering applications. The need of the exercise carried out in this section hence is to optimize the

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material and process parameters to improve the quality of the composite for its applications in gears.

3.8.2 Measure

During this stage, various material and process parameters were measured quantitatively and qualitatively. Performance measures of the existing process were determined by collecting data from the existing compression moulding machine. Figures 3.5 to 3.8 are the main effects diagram showing the performance of moulding and material parameters for r-PET/FAC composite deduced by testing 135 samples. The issues related to the composite are brittle nature of the matrix and debonded reinforcement. The subsequent experimentation brings out the facts that matrix modification with r-LDPE and reinforcement treatment with 3APTMS could resolve the existing issues. Hence M-r-PET/T-FAC composite is taken up for further analysis.

3.8.3 Analyse

In this stage of Six Sigma implementation, the goal is to substantiate a valid relationship between the process parameters and their corresponding response variables. Experiments with M-r-PET/T-FAC composite using L_{27} OA given in the section 2.3 are conducted and the average values of S/N ratios for each response at three levels are calculated and are used in deciding the optimum parameter of the response. The response table and the main effect graphs are given in the Table 3.16 to 3.20 and Figure 3.31, 3.33 to 3.36. The optimum levels for process and material parameters derived from the response graph are tabulated in the Table 3.21.

Table 3.21: Optimum parameters for flexural and wear properties of the composite

Parameter	Strength	Strain	Toughness	Modulus	SWR
Moulding pressure (MPa)	15	15	15	15	15
3APTMS (%)	8	10	8	10	6
R-LDPE (%)	10	30	30	10	20
Moulding Temperature (ºC)	100	150	50	100	150
FAC (%)	15	5	15	15	10

a. Analysis of variance (ANOVA)

An ANOVA analysis is performed to establish the relative significance of the individual factors. The assumptions used in this statistical analysis are

1. The observations at each factor level should be independent of each other.
2. The population variances at each of the factor levels should be the same.
3. The observations from each factor level should follow a normal distribution.

The 27 experiments conducted during compression moulding are random selection of observations. This ensures that the first assumption is being met.

To validate the assumption of equality of population variances, two different tests viz. Bartlett's test and Levene's test are conducted. The null and alternate hypotheses considered are,

H_O = the population variances at each of the factor levels are same.

H_1 = at least two of them differ.

The level of confidence is at 95%. The result of the tests, displayed in the Table 3.22, show clearly that neither of the p-values are below a reasonable error rate (5%), so both tests suggest that the data tends to agree with the null hypothesis (i.e. that the population variances are the same at each of the factor levels) (Neter. J, et al. 1985).

Table 3.22: Bartlett's and Levene's test data

Factor	Bartlett's test		Levene's test	
	Test statistic	p-value	Test statistic	p-value
Moulding pressure	4.92	0.086	2.29	0.123
3APTMS	2.54	0.281	1.33	0.283
r-LDPE	6.14	0.057	1.70	0.204
Moulding temperature	1.78	0.411	1.54	0.235
FAC	2.28	0.321	1.49	0..246

The third assumption is checked using a normal probability plot shown in the Figure 3.41. A normal probability plot is a graph of the cumulative distribution of the residuals on normal probability paper, that is, graph paper with the ordinate scaled so that the cumulative normal distribution is plotted as a straight line. In this Figure

$$P_k = (K - \frac{1}{2}) / N \qquad\qquad (3.1)$$

in which P_k is calculated for the kth point, while there are N data points in total (Montgomery 1991). The observations in this plot fall on a straight line. The P value obtained for the test is 0.817 which is greater than alpha level, 0.05 (level of significance-95% confidence), on this basis it can be said that the data follow a normal distribution validating the third assumption.

The validity of these three assumptions points to the fact that ANOVA analysis can be applied to the set of data generated for optimizing material and compression moulding parameters. Table 3.23 is the ANOVA table in which DOF is the degree of freedom, SS is the sum of squares, MS is the mean squares or estimated variance and F is the variance ratio. After comparing the results by using sum of square and mean square to select the weak effects, Shiau (1989), determined that mean square is a better criterion to pool the weak effects. Smaller the mean square, weaker is the effect.
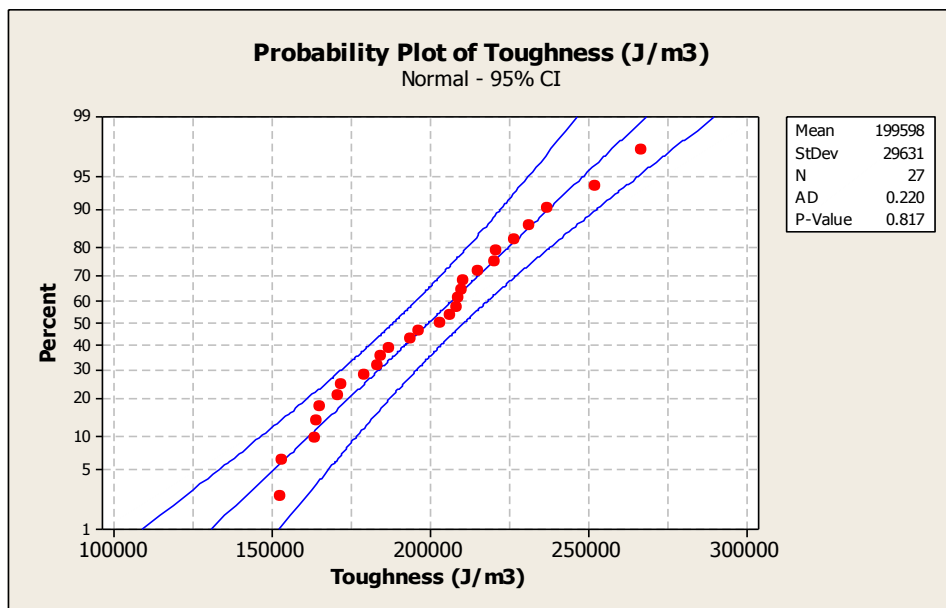
Figure 3.41: Normal probability plots of toughness

Table 3.23: ANOVA analysis illustrating the significance level of various factors for toughness of M-r-PET/T-FAC composite

Factor	DOF	SS	MS	Variance	F-ratio	Percentage Contribution
A	2	39392256	19696128	890277.65	44.25	**18.35**
B	2	11196416	5598208	890277.65	12.58	5.21
C	2	42212352	21106176	890277.65	47.41	**19.66**
D	2	5701632	2850816	890277.65	6.40	2.66
E	2	58793984	29396992	890277.65	66.04	**27.38**
C×D	4	8380416	2095104	1780555.29	4.71	3.90
C×E	4	2215936	553984	1780555.29	1.24	1.03
C×D×E	8	10703872	1337984	3561110.59	3.01	4.99
D×E	4	15770624	3942656	1780555.29	8.86	7.35
C×D^2	8	3689472	461184	3561110.59	1.04	1.72
C×E^2	8	1509990	188749	3561110.59	0.42	0.70
Error	34	15134720	445139			7.05
Total	80	2.15E+08	2683771			100.00

Table 3.23 shows that the weight fraction is the most critical parameter contributing up to 27%. Next is the r-LDPE content and moulding pressure contributing up to 20% and 18% respectively. Further, Table 4.10 illustrates the percentage contributions of the various interaction effects also. Similar ANOVA table for SWR is also constructed and percent contribution of operating and process parameters and their interactions are noted.

The results obtained from the Taguchi experimental design can further be fine-tuned by incorporating response surface methodology (RSM) (Box and Draper, 1987). In this work RSM is implemented to make the analysis more precise and accurate in the improve phase of the Six Sigma implementation.

3.8.4 Improve

In this stage of the Six Sigma implementation, the results obtained from the DOE analysis are further considered for fine tuning of parameters. The main objective is to optimize the settings of the critical parameters. Therefore, response surface methodology (RSM) is employed to establish a robust regression model and find possible optimized results. In the next subsections, the response surface methodology implementation is discussed.

a. *Response surface methodology (RSM)*

The treatment method for RSM for addressing a problem is described in Section 1.8.4. A higher order polynomial as given in the equation 1.13 is employed to search for the general vicinity of the optimum region for toughness and SWR of M-r-PET/FAC composite. Using this equation, quadratic models for toughness and SWR are generated. The objective in this exercise is not only to investigate the response over an entire factor space but also to locate the region where the response approaches its optimum or near optimal value.

b. *Quadratic model for toughness*

All the main parameters and their interactions are included for the initial analysis of the responses obtained from RSM. The model is then reduced by eliminating the terms with no significant effect on the response through the backward elimination process. The final quadratic model of response equation in terms of actual factors is presented in the equation 3.5, below.

Toughness (J/m3) = 293325 + 24309 Pressure (P MPa) - 26593 Silane(S %)

$$- 8530 \text{ r-LDPE (L \%)} - 4254 \text{ Temperature (T } ^\circ\text{C)}$$

$$+ 2891 \text{ FAC (F \%)} - 474 \text{ P}^2 + 5194 \text{ S*F} + 13.2 \text{ T}^2$$

$$- 397 \text{ F}^2 + 89.2 \text{ L*F} + 733 \text{ L*S} + 80.7 \text{ L*T} - 1221 \text{ F*P}$$

$$+ 154 \text{ S*T} - 340 \text{ W*S}^2 - 0.410 \text{ B*T}^2 \tag{3.2}$$

The coefficient R^2 is defined as the ratio of the explained variation to the total variation, and is a measure of the degree of fit for the proposed model. When R^2 approaches unity,

response model fits better with the actual data. The proposed model is found to fit by 95.3% (R^2).

c. *Quadratic model for SWR*

The procedure adopted to develop the quadratic model for toughness, explained in the previous sub section, is followed for generating a similar model for SWR. The resultant quadratic model is given in the equation 3.6.

$$\text{SWR} (*10^{-12}) = -25.1 - 0.126 \text{ Pressure (P MPa)} + 9.34 \text{ Silane(S \%)} - 0.441 \text{ r-LDPE}$$
$$(\text{L \%}) - 0.126 \text{ Temperature (T }^\circ\text{C)} + 7.44 \text{ FAC (F \%)} - 0.571 \text{ S*S}$$
$$- 0.298 \text{ F*F} + 0.0303 \text{ L*S} - 0.0159 \text{ L*P} + 0.00261 \text{ L*T} - 1.62 \text{ S*F}$$
$$+ 0.0112 \text{ F*T} + 0.0858 \text{ F*P} + 0.000568 \text{ L*F}^2 + 0.0751 \text{ F*S*S}$$
$$+ 0.0267 \text{ S*F}^2 \tag{3.3}$$

The proposed model is found to fit by 94.7% (R^2). In order to determine the optimal response point for both toughness and SWR, combined optimization for M-r-PET/T-FAC composite is carried out. The results of such a procedure are explained in the next section. .

3.8.5 Results of combined optimization for toughness and SWR

To determine the optimal parameters for combined responses, overlaid plots are used. The overlaid plots for % FAC, moulding pressure, % 3APTMS, % r-LDPE and moulding temperature are shown in the Figure 3.42. It could be observed from the figure that for toughness in the range 262 to 267 kJ/m^3 and SWR in the range 2 to 5 $*10^{-13}$ m^3/Nm, the optimum parameter settings are as given in the table 3.24.

Table 3.24: Final optimum parameters for better material properties obtained from overlaid plots

Parameter	Level
Moulding pressure (MPa)	11.2
3APTMS (%)	7.9
R-LDPE (%)	29
Moulding Temperature (ºC)	52.6
FAC (%)	12.5
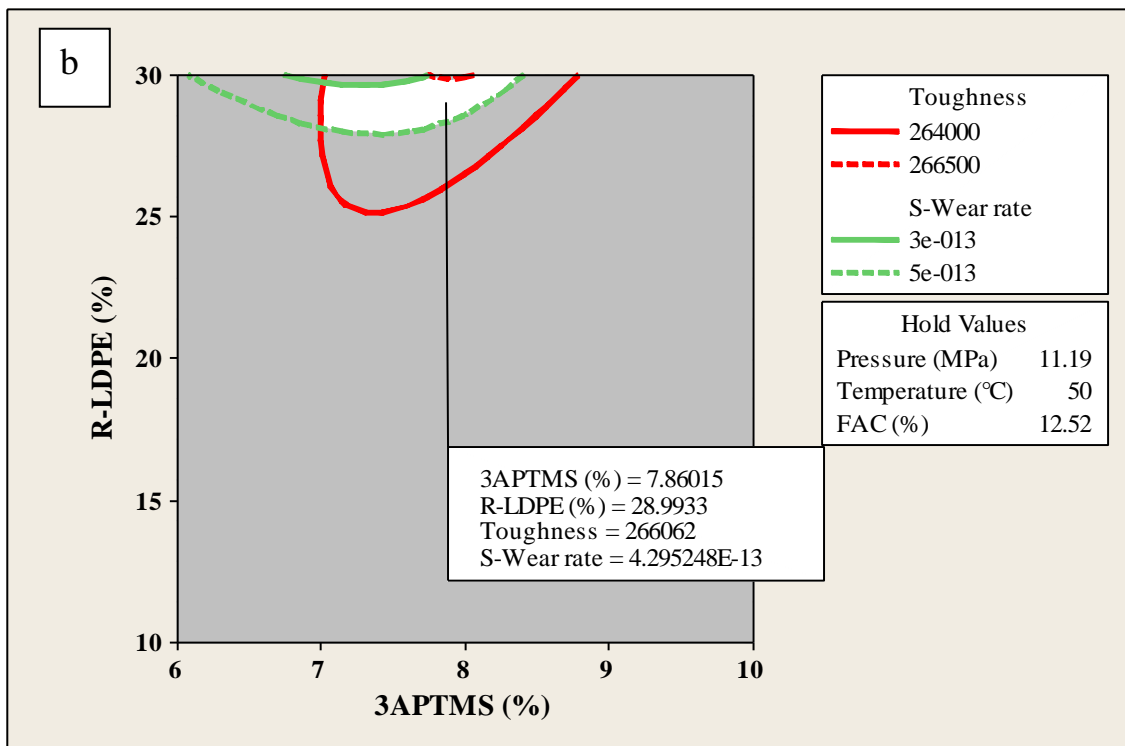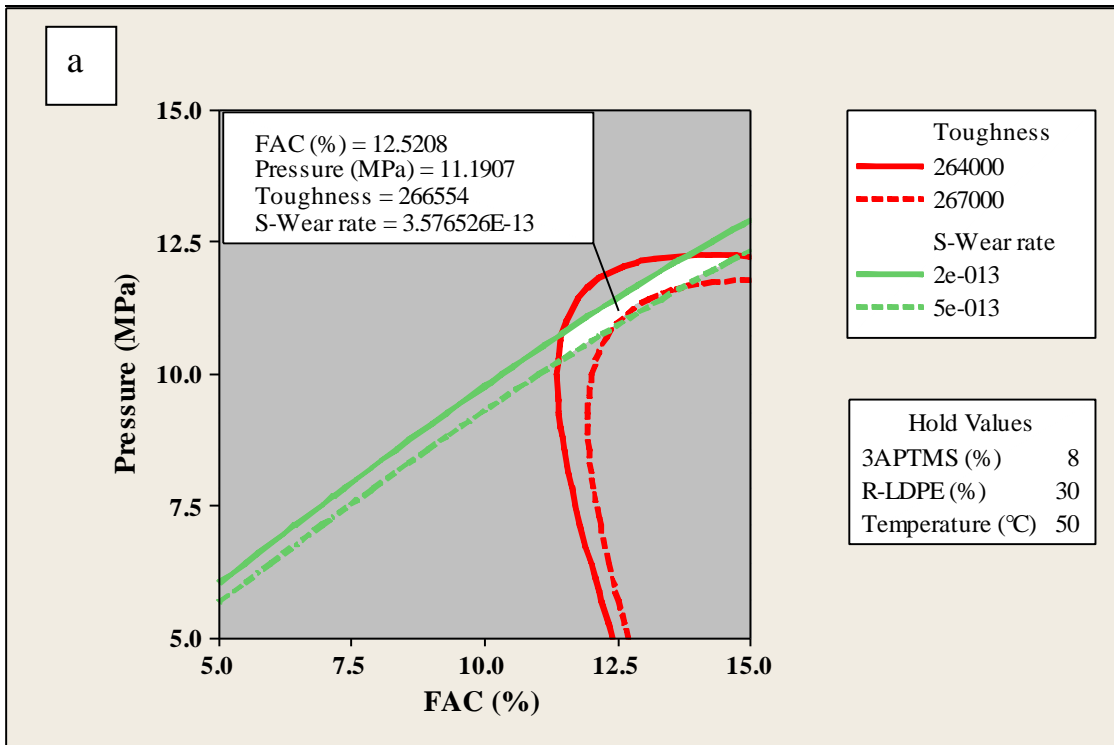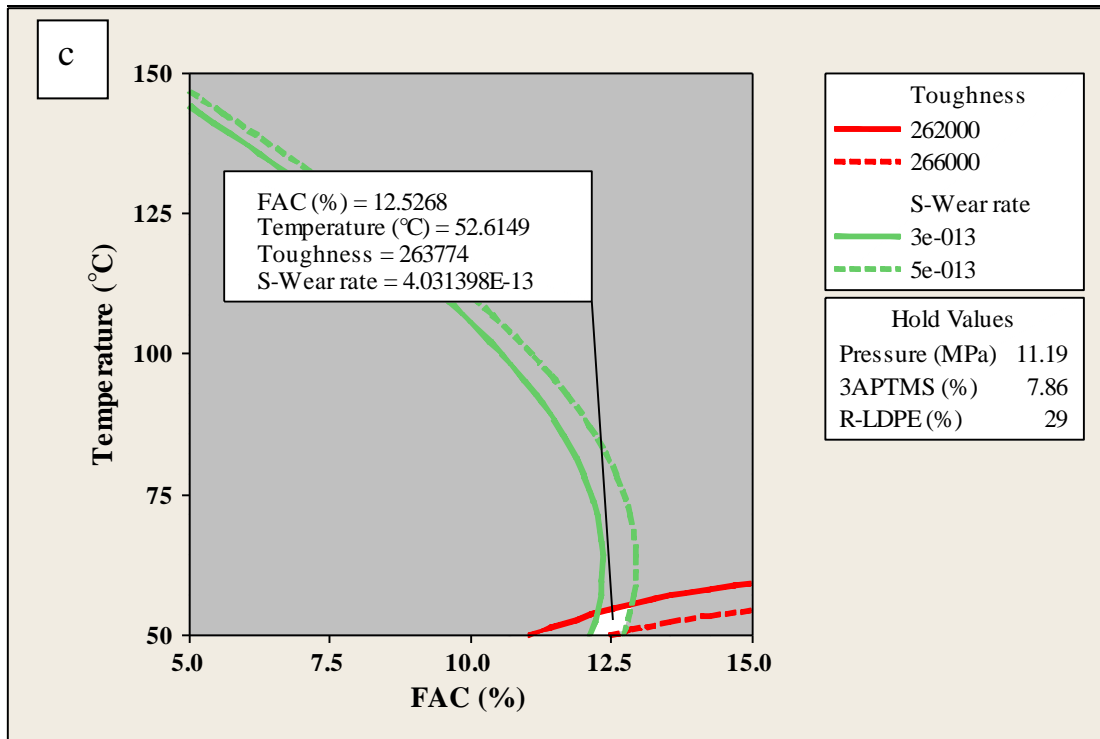
Figure 3.42: Overlaid graphs for toughness and SWR showing optimum (white) regions for material and process parameters

    a.   **Optimization of FAC content and Moulding pressure**

    b.   **Optimization of R-LDPE content and 3APTMS**

    c.   **Optimization of Moulding Temperature**

3.8.6 Control

The Control stage is the last and final stage of Six Sigma implementation. In this step, confirmation experiments are conducted for verifying the predicted quality characteristic by the proposed model with respect to the chosen initial or reference parameter setting. The levels of moulding conditions used for compression moulding operation for the confirmation test are shown in the Table 3.24. The predicted value is evaluated using quadratic equations as given in the Eqn. 3.2 and 3.3. Table 3.25 compares the predicted value for flexural strength with the experimental results.

Table 3.25: Results of confirmation tests

Confirmation test number	Experimental results	Result predicted by quadratic model	Error (%)
Toughness (kJ/m^3)	257	265.44	3.18
SWR (*10^{-13}) m^3/Nm	3.021	2.866	5.41

From the confirmation test results it can be deduced that the developed mathematical model for optimal machine performance of compression moulded recycled PET composite agree well with the experimental tests. The proposed quadratic model is of great importance for the proper selection of control parameters during compression moulding in manufacturing industries.

3.9 RESULTS OF TESTING GEARS MOULDED WITH MATERIAL AND PROCESS DEVELOPED

The details of polymer gear designed for the study are provided in the section 2.2.4. The test gear is of 36 teeth with 1.197 module. The mould used for shaping the gear is shown in Figure 2.10. The driving gear is made of Cast iron having same module and 72 numbers of teeth. the gear test rig utilized for the current work is detailed in section 2.4.3. Five samples are tested in each category and tested at a fixed speed of 250 rpm. Accelerated testing with "Step test method" is carried out where the load on gear incremented by 5 N for every 15,000 rotations as shown in the Figure 2.23.

The composite gears are moulded with the optimum parameter levels tabulated in Table 3.24, using the compression moulding machine. These are tested for their performance and the result of step tests, conducted on r-PET/FAC and M-r-PET/T-FAC gears are shown in the figure 3.43. It can be revealed from the figure that, the gears tested for both composites survive over 10,000 revolutions at loads up to 5N. However, the gear life drops as load acting on the tooth increased. At around 15N load, out of five r-PET/FAC gears, only 20% survive 10,000 revolutions. On the other hand, over 80% of the gears of M-r-PET/FAC, moulded with optimized parameters survive 15N load showing clear

indications of improvements in the performance. Such an observation points to 275% improvement. Further, the gears moulded with optimized parameters depict increase in load handling capabilities. 20% of gears survive 30N load, 60% of gears survive 20N load and 80% of them survive 15N. Such capabilities are not observed in r-PET/FAC gears as can be clearly seen from the figure. These gears could only survive a maximum of 15N load.
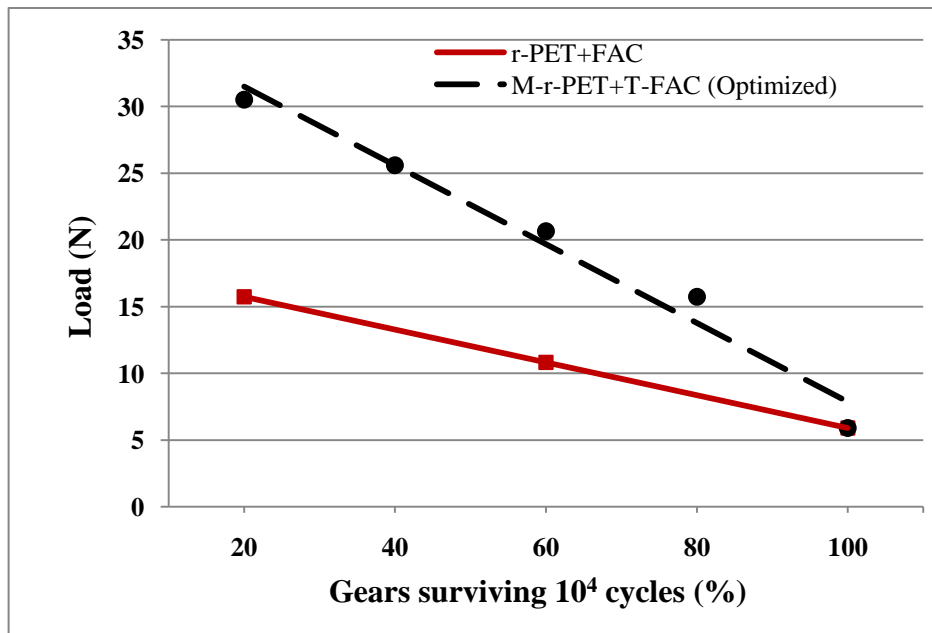
Figure 3.43: Step test results for r-PET composite gears showing improvement in load handling and useful life for developed composite, moulded with optimized process

Thus from Fig. 3.43 it seems that the efforts towards optimizing the moulding process and material parameters are helpful in improving the load bearing capacity and life of the gears.

Conclusions from the present work are elaborated in the chapter to follow.

CHAPTER 4

CONCLUSIONS

A Systematic study is carried out with recycled Poly ethylene terephthalate blended with recycled low density poly ethylene. The blend is reinforced with cenospheres which are treated with 3-amino propyl trimethoxy silane. Six Sigma optimization techniques are utilized for developing compression moulding process as well as optimizing material and process variables. The primary objective of this exercise is to develop r-PET based composite and optimize compression moulding for moulding low cost gears for suitable applications in toys, office machines etc. The results provided in the chapter 3 leads to following conclusions.

A recycling procedure developed to mould r-PET adopting Six Sigma DMADV methodology concludes successful in moulding fairly good samples. Loading r-PET flakes to the hot mould resulted large voids in the sample with Risk Priority Number as high as 900. Grinding flakes and using it for moulding reduces the size of void and RPN to 315. However the sample seemed very fragile and unsatisfactory for engineering applications. Converting the flakes to a mushy form and charging it to the mould reduced RPN to 8 which produced fairly good samples. The process thus developed sees convenient for recycling post consumed PET through thermo mechanical route. The use of DMDV based Six Sigma along with FMEA techniques, found to efficiently address the problem of optimisation of compression moulding.

With the process developed for moulding r-PET, the polymer is reinforced with FAC and investigated for flexural and wear properties. The DOE methodology adapted for such investigations showed a down ward trend for FAC content. The cause investigated using fractographic technique for such a behavior, concludes debonding of FAC from the matrix due to improper interfacial characteristics. Further, the composite underwent brittle fracture making it not much useful for gear applications. The drop in the flexural strength, fracture strain and toughness is the cause of such

characteristic of the material. The remedy considered for developing r-PET composite and make it suitable for the gear application is to blend the matrix with an appropriate recycled polymer and to improve interfacial interactions of FAC with matrix by suitably treating FAC with 3APTMS. The wear property of the composite however, proves promising as FAC reduced SWR. Lubricating action between the composite and the counter face, displayed by hard FAC could be helping the composite in reducing SWR.

In an attempt to reduce the brittle nature of r-PET, it is tested by blending with five softer polymers from recycled arena. R-LLDPE, r-LDPE, r-HDPE, r-PP and r-Nylon are these five polymers. The results displayed by such blends conclude that blending r-PET with r-LDPE shows a considerable improvement in the energy absorbing behaviour of r-PET/r-LDPE blend making it a suitable blending plastic. Blending r-PET with 10% r-LDPE improves the toughness by 100% and by 112% at 30%. This is followed by r-HDPE that shows 25% and 100% increase at respective composition. The improvement in toughness could be the result of adequate strain to fracture, displayed by the blend. At 10% weight, r-LDPE blend shows maximum strain at fracture where as it is second to r-HDPE at 30%. All the five neat r- blends show over 5% of strain at fracture. Reduction in the modulus of the blend is also dropped making the blend more flexible. At 30% concentration, the reduction in modulus is highest with r-LLDPE (83%) and least with r-HDPE (48%). A balance between the flexibility and the stiffness is essential for adapting a material for engineering applications. In this connection, r-LDPE that affects the modulus intermediately (54% drop) thought to be a better selection. Flexural strength and SWR of r-PET/r-LDPE blends affected marginally when compared to the plastics considered in this study. The results of the study show that both at 10% and 30 % of blend in r-PET/ r-LDPE blend display minimum reduction in flexural strength. A marginal increase in the wear of r-PET blends is also observed. The increase in the weight loss of r-PET/r-LDPE blend is observed to be the least and that with r-PET/r-PP blend is highest. The results of SWR conclude that At 10% composition, r-LLDPE display 1.7% higher specific wear rate than r-LDPE, r-HDPE display 53%, r-PP display 79% and r-Nylon display 44% over r-LDPE. Similarly, at 30% composition, r-LLDPE display 31% higher specific wear

rate than r-LDPE, r-HDPE display 25%, r-PP display 147% and r-Nylon display 31% over r-LDPE. The study on flexural and wear behavior of r-PET blends demonstrates that r-LDPE could be a better blending polymer in the group for r-PET.

The results on Flexural properties of M-r-PET/FAC (30% r-LDPE) composites conclude a 53% drop in modulus at 5% FAC composite and the drop is 50% at 15% FAC. Further, matrix modifications indicate a marginal, 17% (average) drop in the strength. However, an improvement in the fracture strain, over 87 % is noted at 30% of r-LDPE and 15% FAC. R-LDPE being more rubbery when compared to r-PET, improves the strain-ability of the composite. 17% decrease in the strength. An improvement in toughness by about 66 MPa at 5% FAC and 13 MPa at 30% of FAC is observed. Thus studies on matrix blending conclude that blending r-PET with r-LDPE helps in reducing the brittleness of r-PET and makes it suitable for engineering applications. Although matrix is developed, unbounded FAC are seen in the SEM pictures. FAC treatments are considered in the next stage.

Reinforcing r-PET with 3APTMS (10% by wt.) treated FAC improved flexural strength of r-PET/T-FAC composite. An increase of 34% strength at 5% T-FAC, 57% increase at 10% and 120% improvement in strength at 15 % of T-FAC is observed owing to surface treatments given to FAC. Such an increase in the properties leads to improvement in the toughness of the composite. Toughness improves by 95% at 5% of T-FAC, 200% at 10% and an increase of 271% in toughness when r-PET is reinforced with 15% T-FAC is observed. Treating FAC also improves modulus marginally. 20%, 1% and 10% increase at 5, 10, 15% T-FAC is observed. A drop in the SWR is resulted due to treatments provided to FAC. 48% drop, 8% and 6% drops at 5, 10 and 15% T-FAC is observed. The results of flexural and wear properties of r-PET.T-FAC composite indicate an improvement in the properties owing to the treatments given to FAC. The SEM micrographs displayed good binding between matrix and reinforcement in a brittle matrix. These results are the comparative results w.r.t. r-PET/FAC composites. In the composite development process both matrix and reinforcement modifications are dealt in the next stage.

Result of M-r-PET/T-FAC composite displayed improvement in strength, fracture strain and toughness. Modulus and SWR however are lower to that displayed by r-PET/FAC composite. The improvement in the flexural and wear properties of the composite due to combined effects of matrix modification and treatment of reinforcement seems appreciable. The results presented about 5%, 40% and 57% hike in the strength at 5, 10, 15% T-FAC composite blended with 30% r-LDPE is observed. 130,241, 323% improvement in fracture strain at different FAC content and 139, 240, 543% improvement in toughness is observed. Modulus and SWR however, dropped on blending and treating. 54% decrease in modulus at all levels of T-FAC is resulted in flexibility of the composite. SWR saw 55%, 25% and 17% decrease on reinforcing blended matrix with 5, 10 and 15% of T-FAC. The results of M-r-PET/T-FAC composite conclude favorably for developing low cost material from recycled means for industries working in the competitive market. In the next stage, the process and material thus developed are optimised for flexural and wear properties.

The optimization of process and material parameters carried out using Six Sigma DMAIC methodology with Taguchi's method. The main effects diagram show upward trend for FAC for the developed material, which was downward prior to the development. The optimum parametric settings for flexural and wear parameters, as displayed in Table 3.21 conclude difference in settings for different parameters. Combined optimization for toughness and SWR using overlaid graphs with RSM concept leads to final optimum parametric settings. The final optimum parameters for moulding r-PET reinforced with FAC are Moulding pressure – 11.2 MPa, 3APTMS - 7.9 % by wt., r-LDPE - 29 % by wt., moulding Temperature - 52.6 ºC and FAC – 12.5%. With optimum levels for material and process parameters developed, the gears are moulded and tested for their performance. The performance of such gears is compared with r-PET/FAC composite gears to investigate the extent of improvements achieved through this work.

The performance of composite gears moulded with optimized parameters seems satisfactory when compared to r-PET/FAC gears. The increase in the gear life by about 275% seems good for the applications sought for them. The gear can handle a

load of about 30.5 N and can take about 50,000 revolutions. With such an improvement shown by the composite material developed in this work, it could be considered as an alternative to the existing gears made from neat polymers for lower loading applications.

The objectives set for this research work was to develop a low cost composite material from environment hazardous waste materials with optimized compression moulding for gear applications are met with the systematic application of Six Sigma methodologies as explained in this work. The outcome of this work provides technical support for applying recycled materials like r-PET, r-LDPE and FAC for low tech engineering applications and has significances in its promotion in the future. Developing composite materials from recycled sources and researching on its applications in wider dimensions will expand the sphere of applications for these materials and solve problems related to the disposal of such environment unsafe materials.

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Krishna Prabhu, B., Chomal, G.J. and Kulkarni, S.M "Investigation on effect of processing parameters on properties of recycled-PET composites using Taguchi method" International conference on education and green sky-materials technology for a better world, SAMPE-13 at Long Beach CA, USA

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