This chapter deals with the general introduction of the study conducted in this thesis. It gives the information on the fillers and polymers used along with their environmental effects and importance of their use in this research work. This chapter also highlights the various aspects polymer composites and their relevance in today’s world. Lastly this chapter discusses in details the research work conducted on fly ash reinforced polymer composites. This chapter also presents the scope of this study and a short summary of the work.
Today’s world is moving towards the development of sustainable materials that are both economically viable and environmentally friendly. An approach has been adopted by scientists where materials are developed from industrial wastes that are generated as a result of anthropogenic activities and affect our environment immensely. The abundance of these materials on this planet creates an urge to ‘recycle and reuse’ them in making value-added materials with advanced properties. A lot of research has been carried out in the past decades where materials have been structured by incorporating reinforcing fillers in polymer matrices. Such polymer materials when collected from recycled or waste industrial products render both environmental and economical sustainability to it. Thus, development of value-added materials from recycled post consumer plastic products such as recycled polyolefins (polypropylene, polyethylene etc.) reinforced with filler/s is an interesting approach. In this regard, the thermal power plant (TPP) byproduct fly ash has been chosen as a filler which when used as reinforcement render environmental sustainability to the recycled polymer composites. A brief insight into fillers and the polymers used in the study and the environmental problems incurred by them are discussed.
1.1 Fly ash

Fly ash is a coal combustion by-product and constitutes about 85% of the total residue generated from coal combustion processes having harmful environmental effects such as air pollution and groundwater contamination due to leaching of heavy metals present in fly ash deposits when disposed openly in the environment [Iraola-arregui et al., 2011; Ma et al., 2007]. In the thermal power plants (TPPs), it is extracted by the precipitators in the smokestacks to reduce pollution and facilitate its way for further utilization. A brief overview of fly ash generation and route to disposal and utilization is given in Figure 1.1.

Figure 1.1: Fly ash generation and route to disposal and utilization
1.1.1 Classification and Composition of Fly ash

According to ASTM C-618 fly ash is broadly classified into two major categories: Class F and Class C. The main difference between these two classes is due to the amount of the oxides of calcium, silica, alumina and iron present in the fly ashes. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (i.e., anthracite, bituminous, and lignite).

Class F fly ash: The burning of old anthracite and bituminous coal typically produces Class F fly ash which contains less than 10% lime (CaO).

Class C Fly ash: This type of fly ash is produced from the burning of younger lignite or sub bituminous coal generally containing more than 20% lime (CaO) [Alam et al., 2011].

Figure 1.2: Classes of fly ashes: a. Class F fly ash, b. Class C Fly ash

Fly ash particles are generally spherical in shape and range from 0.5 μm to 100 μm in diameter and consist mostly of silicon dioxide (SiO\textsubscript{2}), which is present in two forms: amorphous, which is round and smooth, and crystalline which is sharp pointed and hazardous; aluminium oxide (Al\textsubscript{2}O\textsubscript{3}) and iron oxide (Fe\textsubscript{2}O\textsubscript{3}). They also contain
some environmental toxins like arsenic, cadmium etc. depending upon their presence in the coal bed [Haque et al. 2013]. The detailed chemical composition of Class F fly ash used in this study will be given in Chapter 2.

![Figure 1.3: a: Bulk fly ash; b: SEM micrograph of fly ash particles](image)

**Figure 1.3:** a: Bulk fly ash; b: SEM micrograph of fly ash particles

### 1.1.2 Fly ash production, utilization and the current environmental scenario with an Indian overview

Fly ash production as thermal power plants (TPPs) byproduct is prevalent in the world especially in the developing countries. A comparative account of the fly ash production in the world is given in **Table 1.1.**
Table 1.1: Fly ash generation and utilization in different countries [Alam et al., 2011]

<table>
<thead>
<tr>
<th>S. No</th>
<th>Country</th>
<th>Annual ash production, Million tonne (MT)</th>
<th>Ash utilization %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>India</td>
<td>112</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>China</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>USA</td>
<td>75</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>Germany</td>
<td>40</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>UK</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>Australia</td>
<td>10</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>Canada</td>
<td>6</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>France</td>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>9</td>
<td>Denmark</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>Italy</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>Netherland</td>
<td>2</td>
<td>100</td>
</tr>
</tbody>
</table>

In India up to 2011, 120 coal based thermal power stations were producing nearly 112 million tonne (MT) fly ash per year [Alam et al., 2011] and in the financial year 2016-17, it is expected that the production of fly ash will increase to around 300-400MT/year [Alam et al., 2011; Haque et al., 2013]. The large amount of fly-ash produced if not utilized in right quantity will be hazardous to the environment. With the increasing demand of power and coal being the major source of power, more and more thermal power stations are expected to be commissioned/augment their capacities in near future. Fly ash has been considered as a “Pollution Industrial Waste” till about a decade back and was being disposed off in ash ponds. Indian coal has high ash content (35%-45%) and low calorific value (3500 kcal/kg – 4000 kcal/kg) as a result of which huge quantity of fly ash is generated. This would require about 4000 hectare of land for the construction of ash ponds. Out of the total power generated in India, about 70% is produced from thermal power plants (TPPs). The majority of the thermal power plants (about 84%) is run by coal; rest on gas
(13%) and oil (3%). Thermal power plants use 260 MT of coal which is about 65% of annual coal produced in India generating huge amount of fly ash as by product [Alam et al., 2011].

Along with reduction in the production of fly ashes, there is also a need to utilize this industrial hazardous waste as a resource by developing novel ideas of its usage in an economical and environmentally sustainable manner.

Fly ash has proven its suitability for variety of applications as admixture in cement/concrete/mortar, lime pozolana mixture (bricks/blocks) etc. Cement and concrete industry accounts for majority of fly ash utilization followed by low lying land fill, roads & embankments, dyke raising, brick manufacturing and other new areas for safe disposal of fly ash are in paint industry, agriculture etc. [Alam et al., 2011]. India achieved utilization 54.33 percentages in 2012 which was significantly higher than the previous amount reported in Table 1.1. However, it would require lot of effort to achieve 95-100 percentage utilization. Concentrated efforts have been made by Department of Science and Technology, Government of India to increase the scale of utilization of fly-ash [Haque et al., 2013].

According to Central Electrical Authority (CEA), Govt. of India and based on the information collected from thermal power stations in the year 2012-13, the fly ash utilization modes are shown in Figure 1.4 [Loya et al., 2014].
Figure 1.4: Modes of fly ash utilization and the percentage of the utilized fly ash in each mode [Loya et al., 2014]

Similarly, research work has been conducted worldwide in utilizing fly ash as an attractive filler in polymer matrices like natural rubber, unsaturated polyester resins, vinyl ester resins, polyethylene, polypropylene etc. in order to develop composite materials with enhanced properties having various application potential [Guhanathan et al., 2004; Sridhar et al, 2009; Nath et al., 2010a].
1.2 Recycled Polymer

Since 1940s when the first industrial scale production of synthetic polymers (plastics) took place, the production, consumption and generation rate of plastic solid waste (PSW) has increased considerably. Plastics are used in our daily lives in number of applications ranging from manufacturing products which are used for coatings, wiring, packaging to development of materials such as, films, covers, bags containers, electronics etc. They are also used for agricultural purposes like making mulches and developing greenhouses [Al-Salem et al., 2009]. Once hailed as a 'wonder material', plastic is now regarded as a serious worldwide environmental and health concern essentially due to its non-biodegradable nature. Careless disposal of plastic bags chokes drains, blocks the porosity of the soil and causes problems for groundwater recharge [Kumra et al., 2002; Narayan et al., 2001]. In India plastic solid waste is an important environmental concern due to reasons like plastic content of the municipal waste is picked up by rag pickers for recycling either at primary collection centers or at dumpsites which is a non formalized profession and has huge shortcomings and results in littering which leads to choking of drains, streams, etc. As a result of which Indian government has formulated various rules and have undertaken various initiatives for plastic recycling and utilization of recycled plastic materials. Thermoplastics contribute to the total plastic consumption by roughly 80%, and are used for typical plastics applications such as packaging but also in non-plastics applications such as textile fibres and coatings [Dewil et al., 2006]. Among the post consumer thermoplastic products, the largest fraction is mostly comprised of polyolefins such as polypropylene and polyethylene (60-70%) and the remaining include polystyrene (10-15%), polyvinyl chloride (15%) and polyethylene terephthalate (5%) [Deepthi et al., 2010]. Increasing cost and decreasing space of
landfills are forcing considerations of alternative options for plastic solid waste disposal [Zia et al., 2007]. The plastic industry has successfully identified workable technologies for recovering, treating, and recycling of wastes from discarded products. For example in 2002, 388,000 tonnes of polyethylene (PE) were used to produce various parts of textiles, of which 378,000 ton were made from PE discarded articles [Al-Salem et al., 2009].

Among the plastic wastes, polypropylene, a linear hydrocarbon polymer, is found in high concentrations in the plastic wastes as mentioned earlier. Among the different types of polypropylene (PP), isotactic polypropylene is most widely used on a commercial scale and so is the type predominant in plastic wastes. The amount of energy consumed in polypropylene recycling process is lower than the energy required for the production of new materials. It is one of the least expensive plastics to make but the process of recycling the plastic is less efficient than other plastics having products with little end value.

Again, polyethylene which is another important polyolefin is the most common plastic. The annual global production is approximately 80 million tonne [Piringer et al., 2008]. Its primary use is in packaging (plastic bag, plastic films, geomembranes, containers including bottles, etc.). Thus, recycled polypropylene and polyethylene were chosen as the polymer matrices in this study. Development of value-added products from recycled polymers is required in order to ascertain their effective re-use.
**1.3. Polymer composites - a general idea**

Composites are made by combining two or more materials to give a unique combination of properties with reinforcements like fibers, woven or non-woven fabrics, particulates, or whiskers. Use of fillers at optimum percentages result in engineered composite materials having tailor-made properties which includes enhancement in the properties of the existing polymer or incorporation of any other desired property.

Use of inorganic particulate fillers like micro-/nano-SiO$_2$, glass, Al$_2$O$_3$, Mg(OH)$_2$ and CaCO$_3$ particles, carbon nanotubes and layered silicates, are often added to process polymer composites in order to cope with the obvious limitations of polymers, for example, low stiffness and low strength, and to expand their applications in different sectors. This combines the advantages of their constituent phases by modifying the physical and mechanical properties of polymers in many ways [Fu et al., 2008].

Many studies have been conducted on the mechanical properties of these particulate-filled polymer composites. Stiffness or Young’s modulus can be readily improved by adding either micro- or nano-particles since rigid inorganic particles have high stiffness than polymer matrices. However, strength strongly depends on the stress transfer between the particles and the matrix. For well-bonded particles, the applied stress can be effectively transferred to the particles from the matrix; this clearly improves the strength of the composites [Fu et al., 2008].

Thus, requirement of novel particulate filler-matrix combinations is a sought after area for researchers and fly ash might be a viable option. Use of fly ash as
reinforcement in metal matrix composites like in aluminium alloy rendering improved hardness and wear resistance have been reported earlier. Similarly improvements in the yield strength and Young’s modulus of fly ash filled polymer matrix composites have also been reported [Rohatgi et al., 2009]. A literature review on the development of fly ash reinforced polymer matrix composites is given below.

1.4 Fly ash reinforced polymer matrix composites: Literature Review

Ramakrishna et al., [2005a] compared the tensile and flexural properties of unsaturated polyester/fly ash composites with that of unsaturated polyester/granite powder composites and reported that the properties of granite powder/polyester composites were superior to that of fly ash/polyester composites. Kishore at al., [2005] carried out compression strength testing of saline water exposed epoxy systems containing fly ash particles. They observed that the extent of moisture ingestion increased with larger fly ash content in the composites and the strength deceased in the wet composites showing interfacial debonding around the ash particles. Ramakrishna et al., [2005b] also studied toughened epoxy matrix with 4 wt% poly(methylmethacrylate) (PMMA) and reinforced the blend matrix with fly ash particles resulting in highest improvement in tensile and flexural strength in case of 40 wt% fly-ash-filled composites. Sombatsompop et al., [2004] reported a comparative study on the use of fly ash and precipitated silica as fillers in rubbers. They observed discrepancies in the results between precipitated silica and fly ash silica for different rubber matrix systems and concluded that the filler-filler interactions, actual rubber content in the vulcanizates and the particle size of the fillers were responsible for such discrepancies [Sombatsompop et al., 2004].
Menon et al., [2006] investigated the use of fly ash as a filler in natural rubber in presence of 5-10 phr of phosphorylated cardanol prepolymer (PCP) and hexamethylenetetramine cured PCP which resulted in higher thermal stability along with improvement in mechanical properties. Sridhar et al. [2009] reported an increase in tensile properties at lower loading of fly ash in fly ash/waste tire powder/isotactic PP composites. Dynamic mechanical properties of the composites showed the usefulness of fly ash composites in dynamic applications. Thermal properties showed an increase in thermal stability with increasing fly ash content [Sridhar et al., 2009].

Ray et al., [2006a] studied the changes in the mechanical properties of the vinylester resin matrix composites which were fabricated with 30, 40, 50 and 60 wt% of fly ash loading by room temperature casting method. The study reported that fly ash can be used effectively to increase the rigidity and stiffness of the vinyl ester resin matrix, however there was a lowering in the value above 50 wt% of fly ash loading. In a separate study, these composites showed faster thermal degradation at a lower temperature, particularly in case of the 30 wt% and 60 wt % composites and a higher onset temperature for the 40 wt% and 50 wt% composites [Ray et al., 2006b]. Ray [2009] made an attempt to develop fly ash filled polymer matrix composites with high damping behaviour. Unsaturated polyester resin (UPE) was blended with SBR latex in three proportions and this blend was used as the matrix for making 40 and 50 wt% fly ash loaded blend matrix composite. The presence of latex particles significantly enhanced the damping property especially in UPE/10 wt% SBR latex blend matrix having 50 wt% fly ash loading [Ray et al., 2009]. Setsuda et al., [2012] studied the effects of fly ash in low density polyethylene (LDPE) and polypropylene (PP) matrix composites fabricated by injection moulding. The addition of raw fly ash in LDPE caused a decrease in the shrinkage ratio, and increased the bending strength and
flexural modulus. The ground fly ash particles were found to produce better results than the raw fly ash particles in PP composites. The addition of ground fly ash in PP composites caused a decrease in the shrinkage ratio and an increase in the flexural modulus [Setsuda et al., 2012]. Usta [2012] investigated the fire behaviour of rigid polyurethane foams containing fly ash where improvement in the thermal stability of FA reinforced foams in comparison the pure rigid polyurethane was found.

According to Yu-fen et al., [2006] improvement of composite strength by using fly ash as filler has problems regarding the weak interfacial bond between untreated fly ash and polymer. So, modification of fly ashes has been done by various techniques where either coupling agents or surfactants have been added to modify the surface characteristics of the fly ash filler and to improve interfacial bonding within the matrix [Yu-fen et al., 2006]. Kulkarni and Kishore [2002] studied the effects of surface treatments and size of fly ash particles on the compressive properties of epoxy based particulate composites where the microscopic observations of compression tested samples revealed a better adherence of the particles with the matrix in case of treated particles and regarding the size effect, the composites with lower average particle size showed improved strength at higher filler contents. Kishore et al., [2002] also studied the impact behaviour of epoxy specimens containing 10% by volume of fly-ash particles with their surface treated for improving or decreasing adhesion. It was noticed that samples involving adhesion-increasing treatments (use of silane) show greater absorption of energy and maximum load compared to untreated samples and those subjected to adhesion-reducing treatments. [Kishore et al., 2002] Bose et al., [2005] studied the effect of fly ash on the mechanical, thermal, dielectric, rheological and morphological properties of filled nylon 6. They reported that larger particle sized fly ash showed more improvement in mechanical properties compared
to the smaller sized particles, whereas the smaller sized particles showed more improvement in dielectric properties compared to the larger sized particles. They also concluded that the rigidity, heat stability and dimensional stability of the composites were enhanced on addition of fly ash to nylon 6 matrix and found that titanate coupling agent played a significant role in improving the mechanical properties of the composites [Bose et al., 2005]. The physical properties of silanized and unsilanized fly ash filled unsaturated polyester composites in both uncured and cured states were reported [Sen et al., 2000]. They observed a lower cure rate in silanized fly ash filled composites and a higher cure rate in unsilanized fly ash- filled composites compared to the neat resin [Sen et al., 2000]. Nath et al., [2010a] chemically modified fly ashes by activation with sodium hydroxide and used it in fabrication of bio-composite films with poly(vinyl alcohol) (PVA) by aqueous casting method. The composite film reinforced with 20 wt% modified fly ash showed up higher tensile strength 289% (three-fold) compared to those of unmodified FA filled films [Nath et al., 2010a]. Nath et al., [2010b] reported that the use of sodium lauryl sulphate (SLS) coupling agent resulted in 33% higher strength in SLS modified FA/PVA films than that of FA/PVA films. This phenomenon was attributed to an enhanced physical bonding between FA and PVA in presence of SLS [Nath et al., 2010b]. According to Parvaiz et al., [2011] in vinyltrimethoxy silane and 3-aminopropyltriethoxy silane modified fly ash reinforced polyetheretherketone (PEEK) composites, improved mechanical and thermal properties were observed than that observed in the unmodified FA/PEEK composites. The increment of the dynamic modulus for the PEEK/treated fly ash composites was 32% at 250°C, indicating apparent improvement of high temperature mechanical properties [Parvaiz et al., 2011]. Bonda et al., [2012] studied the viscoelastic, mechanical, thermal properties, and did microstructural analysis of
Acrylonitrile butadiene styrene (ABS) reinforced with various surface treated fly ash (FA). FA particles were surface treated with various chemical reagents, i.e., Ca(OH)$_2$, NaOH, and Bis (3triethoxysilylpropyl) tetrasulfane (Si69) to improve the interfacial adhesion between ABS and FA. DMA tests confirmed an increase in stiffness in the surface treated composites. TGA also showed higher thermal stability of ABS/FA composites than virgin matrix with the surface treatments of FA. The treated FA composites also showed improved mechanical properties compared to untreated FA composite [Bonda et al., 2012]. Kulkarni and Mahanawar [2013] reported maleic anhydride–grafted polypropylene (PP-g-MAH) as a polymeric compatibilizing agent on various properties of fly ash (FA)-filled polypropylene (PP) composites. The FA content was varied from 0 to 40 wt%. The effect of polymeric compatibilizing agents with different melt flow index (MFI) and very high maleic anhydride (MAH) content on filler/matrix interfacial adhesion and filler dispersion were studied. The values of yield stress and breaking strength of compatibilized PP/PP-g-MAH/FA-based composites showed higher values compared to that of untreated FA-filled PP composites at equivalent filler content. Incorporation of FA into PP led to stiffer materials, as tensile modulus increased significantly. It was also found that heat-deflection temperature and vicat softening point improved with the addition of FA filler. The use of PP-g-MAH as polymeric coupling agent provided improvement in mechanical and thermal properties of filled polymers. The higher effect of compatibilization is obtained using high-molecular-weight PP in PP-g-MAH as a polymeric compatibilizing agent and low-molecular-weight PP in PP-g-MAH resulted in better dispersion of FA in PP matrix [Kulkarni and Mahanawar, 2013]. Kulkarni and Mahanawar [2014] studied the effect of treatment of 0.5, 1.5, and 2.5% titanate-coupling agent (LICA 38) on various properties of fly ash–filled polypropylene (PP)
composites. The fly ash content varied from 0 to 30 wt%. The mechanical and thermal properties of the composite material were evaluated, and microstructure investigated through scanning electron microscopy. The values of yield stress and breaking strength of treated fly ash–based composites showed higher values compared to that of untreated fly ash–filled PP composites at corresponding filler content. It was also found that Vicat softening point improved with the addition of fly ash filler. Morphological studies of the tensile fracture surfaces of the composites revealed that the presence of titanate-coupling agent increased the interfacial interaction between fly ash and PP. It also improved the dispersion of fly ash in PP matrix [Kulkarni and Mahanawar, 2014]. Patil et al., [2014] studied the incorporation of the surfactant sodium lauryl sulphate (SLS) modified nanostructured fly ashes in ethylene-octene copolymer. The surface modification resulted in better interfacial adhesion between the modified fly ashes and the polymer and led to improved mechanical properties [Patil et al., 2014].

Pardo et al., [2010] reported improved stiffness and strength in fly ash loaded/isotactic PP composites where silane coupling agents with amine (GF96) and vinyl (Z-6032) functional groups were used. In contrast, when the coupling agent had a vinyl-benzylamine group no significant differences between the treated composite and the composite with untreated ash was observed. Thermal properties also improved in presence of the coupling agents [Pardo et al., 2010]. Iraola-Arregui et al., [2011] evaluated the role of four coupling agents Lubrizol Solplus C800 (C800), N,N’-(1,3-phenylene) dimaleimide (BMI), γ-methacryloxypropyltrimethoxysilane (γ-MPS) and maleic anhydride –grafted PP (MAPP) in 50 wt% fly ash reinforced PP composites. The C800 modification exhibited the highest strength and toughness balance at 50 wt % loading of fly ash; however the other three coupling agents showed improved filler-
matrix interaction during surface modification analysis [Iraola-Arregui et al., 2011]. In a separate study by the same group high melt, thermal and photo-stability of the composites were observed in presence of the previously mentioned coupling agents [Liauw et al., 2014]. Das et al., [2009] reported utilization of recycled polypropylene by forming composites with fly ash in 1:1 ratio and using two types of coupling agents (silane coupling agent vinyltrimethoxysilane (VTMO) and maleated polypropylene, Epolene G3003). Flexural, water absorption and thermal behaviour improved in composites where VTMO was used as the coupling agent [Das et al., 2009]. Thus, coupling agent treated or surface modified fly ash particle did enhance the mechanical and thermal properties of the fly ash reinforced polymer composite materials.

1.5 Need for using novel coupling agents in fly ash reinforced polymer composites

It is known from the work carried out in the field of fly ash reinforced polymer matrix composites that to incorporate hydrophilic fly ashes into a hydrophobic polymer matrix, surface modification of the fly ash particles is required to achieve an optimum filler/matrix interaction. The most common coupling agent used for this purpose are the silanes and the titanates [Bose et al., 2005; Das et al., 2009; Pardo et al., 2010; Parvaiz et al., 2011; Iraola-Arregui et al., 2011; Kulkarni and Mahanawar, 2014]. These are mainly bifunctional compounds composed of two functionally active end groups, for example silanes like Si-69 and Si-264, consisting of a readily hydrolysable alkoxy group and a relatively non-polar organo-functional group which is compatible with the polymer matrix [Sae-oui et al., 2006]. These coupling agents thus act like a bridge and achieve an effective bonding between the
hydrophilic filler and the hydrophobic matrix by using its bifunctional groups at the two ends.

These silane and titanate coupling agents are expensive chemicals and their synthesis processes have been proven to be hazardous with reports of accidents in plants where they were being produced [Sae-oui et al., 2006; Chen et al., 2002]. So, there is a need for alternative coupling agents which does have the properties similar to these chemicals but are green in nature synthesized through a non-hazardous route and are less expensive. Stearic acid, a saturated fatty acid, has been used as surface modifier for fillers such as nano alumina in EPDM composites [Wang et al., 2011], for calcium carbonate nanoparticles in polypropylene matrix [kamal et al., 2012] and for surface coating fly ashes in polypropylene/ethylene vinyl acetate/high density polyethylene composites [Yao et al., 2013].

In this study, the main objective was to develop value-added composites from two industrial wastes i.e. fly ash and recycled polymer (polypropylene), using four different types of unconventional, renewable, green coupling agents like lauric acid, palmitic acid, stearic acid and an ester of palmitic acid, furfuryl palmitate in place of the conventional silanes and titanates.

1.6 Saturated fatty acids used as coupling agents in this study

The fatty acids used in this study are the medium chain length lauric acid (12C) and the long chain, palmitic and stearic acid (16C and 18C). Brief descriptions of these acids are given in Table 1.2.
Table 1.2: Fatty acids used as coupling agents

<table>
<thead>
<tr>
<th>Name</th>
<th>Number of Carbon</th>
<th>Chemical Formula</th>
<th>Common Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric Acid</td>
<td>12</td>
<td>CH₃(CH₂)₁₀COOH</td>
<td>palm kernel oil, animal milk (goat, cow)</td>
</tr>
<tr>
<td>(dodecanoic acid)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palmitic Acid</td>
<td>16</td>
<td>CH₃(CH₂)₁₄COOH</td>
<td>palm oil, palm kernel oil</td>
</tr>
<tr>
<td>(hexadecanoic acid)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>18</td>
<td>CH₃(CH₂)₁₆COOH</td>
<td>Animal fat, vegetable oils</td>
</tr>
<tr>
<td>(octadecanoic acid)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Furfuryl palmitate, an ester of palmitic acid, was also used as a coupling agent in this study [Mistri et al., 2010]. The chemical structures of these fatty acids are given in Figure 1.5.

Figure 1.5: Chemical structure of the coupling agents used in this study
A probable mode of mechanism of the fatty acids used as coupling agent in a composite system (to be studied here) having the hydrophilic filler fly ash in the hydrophobic polymer matrix. is given in Figure 1.6.

**Figure 1.6:** The probable mode of interfacial interaction by the fatty acid (here stearic acid is shown) with fly ash and polypropylene

1.7 *New application potential of fly ash as filler*

Fly ash has proven to be a filler capable of imparting structural changes, enhancing mechanical and thermal properties in polymer matrix composites. The role of novel coupling agent in fly ash filled recycled polymer matrix composites will be widely studied here.
Researchers are in constant search for novel materials with multiple application potential. So, there is a need to use fly ashes in newer application areas. One of the emerging field of applications of polymer composites is in the development of electrically conducting composite materials which are considered to be relatively inexpensive material for many engineering applications such as electrically conducting adhesives, sensors, actuators, antistatic coating films, thermal interface materials etc [Ma et al., 2009]. There are few reports on the electrical properties of fly ash reinforced polymer composites.

1.8 Electrical properties of fly ash reinforced polymer matrix composites: Literature review

Bose et al., [2005] reported the dielectric properties of fly ash and titanate coupling agent coated fly ash filled nylon 6 polymer composites. The dielectric strength of the neat polymer increased with increasing filler concentration but a variation in dielectric strength was observed in the surface coated (60 and 8 μm sized) fly ash filled composites which was not observed in the uncoated ones. In both the cases dielectric strength increased progressively up to 20 wt% loading of fly ash and then showed a decreasing trend up to 40 % filler loading [Bose et al., 2005]. Raghavendra et al., [2003] carried out in situ polymerization of aniline in presence of fly ash to synthesize polyaniline/fly ash (PANI/FA) composites. The a.c. conductivity of these composites has been found to be in the range of $10^2$ to $10^6$ Hz. The PANI/FA composites showed a sudden fall in the conductivity ($10^6$ s/cm) to ($10^4$ s/cm) in comparison to pure PANI but increased in 20 wt% FA reinforced PANI composites with consequent drop at the higher percentages of reinforcement. The investigations further revealed presence of polarons and bipolarons to be responsible for frequency
depended a.c. conductivity of these composites. The Cole-Cole plots indicated clear shift in the distribution of relaxation times as the wt% of FA in PANI changed [Raghavendra et al., 2003]. Chand et al., [2006] developed functionally gradient epoxy resin having different weight percentages of fly ash. It was observed that the dielectric constant (\(\varepsilon\)) and tan \(\delta\) increased with rise in temperature and decreased with increase in frequency. The a.c. conductivity increased with increase in temperature and frequency. They also hypothesized that the increase in weight percentage of fly ash increased the compaction of fly ash which subsequently increased the values [Chand et. al., 2006]. Ray et al., [2006] measured the temperature dependent resistivity of the unfilled vinylester resin, 30 and 60 wt% fly ash filled vinylester resin matrix composites which showed semiconducting nature in the temperature range of 40-60\(^\circ\)C [Ray et al., 2006]. Narayan et al., [2012] reported the synthesis of polyaniline (PAni) based composites by incorporation of various fractions (20 to 60% by weight) of insulating fly-ash (FA) in semiconducting PAni host. In general, a.c. conductivity (\(\sigma_{ac}\)) of the composites further increased with the fraction of FA due to increasing compactness of the conductive matrix in their presence [Narayan et. al., 2012]. Sharma et al., [2012] studied the dielectric properties of cenosphere filled low density polyethylene (LDPE) composites with varying filler percentage in the temperature range of 34-110\(^\circ\)C. The appearance of peak in the dielectric loss curves for all concentrations confirmed the presence of relaxing dipoles in the cenosphere/LDPE composites. The dielectric constant was found to decrease gradually with increase in filler percentages [Sharma et al., 2012].

Thus fly ashes do play a role in the electrical properties but it does so either in presence of a conducting matrix or when hollow cenospheres separated from bulk fly ashes are used in an insulating polymer matrix.
In this work, an attempt has also been made to investigate the performance of fly ash/carbon black filled hybrid PE composites which might find electrical applications.

1.9 Choice of Carbon black as the second filler

It is well known that carbon black when incorporated in critical amount, referred to as the percolation threshold, impart conductivity to the insulating polymer matrices [Fujikura et al., 1989; Yui et al., 2006; Al-Saleh et al., 2008]. Their incorporation in polymer matrices leads to the development of composites having many diverse applications such as antistatic materials, electrostatic dissipation (ESD) and electromagnetic interference (EMI) shielding etc. These materials have many advantages over traditionally used conductive materials like metals in terms of corrosion resistance, adaptability to application needs, light weight, processability and cost. Different types of carbon fillers (e.g. single walled and multiwalled carbon nanotubes, graphene and carbon black) have been extensively used in commercial production of packaging materials for ESD applications. CB has a significant cost advantage over the highly conductive carbon materials like carbon nanotubes, and chemical stability and weight advantage over metallic fibres, flakes and powders [Al-Saleh et al., 2008].

1.10 Carbon black-the filler

Carbon black (CB) is a material produced from the incomplete combustion of heavy petroleum products such as coal tar, ethylene cracking tar and a small amount from vegetable oil. Carbon black is a form of paracrystalline carbon that has a high surface area to volume ratio. Carbon black when free is environmentally hazardous.
and may produce discomfort to the upper respiratory tract. Carbon black is produced in large amount around the world due to its extensive use as pigment and as reinforcement in automobile tyres, in ink and paint industries. It is also used in electronics and CB from vegetable oil is used in food coloring. In 2011, the Canadian government after an extensive review concluded that under permissible limit and form CB is safe enough to enter the environment. [http://www.ec.gc.ca]

The percolation threshold of CB- filled conductive composites depends on the CB structure (particle size, aggregate shape and structure, porosity and surface chemistry) and on polymer characteristics (chemical structure and crystallinity), on processing methods and use of low amount of CB to reach the percolation threshold is attempted by the researchers [Cui et al., 2007].

![SEM micrograph carbon black (BLACK PEARLS® 2000)](image)

**Figure 1.7:** SEM micrograph carbon black (BLACK PEARLS® 2000)

A brief literature review on CB filled polymer matrix composites is given.
1.11 Carbon black filled polymer matrix composites: Literature Review

Carbon black is an electrically conducting filler used in various insulating polymer matrices like polyethylene, polypropylene etc. [Fujikura et al., 1989; Al-Saleh et al., 2008]. CB particles were reported to be capable of self agglomeration to form conductive networks and percolation is delayed by the bulk mobility of polymer layers surrounding the CB particles. This is often achieved by incorporating CB as conducting filler in various blends of polymers aiming at reducing its percolation threshold [Yui et al., 2006]. Tchoudakov et al., [1996] reported the electrical resistivity and morphology of CB filled polypropylene/nylon (PP/Ny) immiscible blends. CB was found to be preferentially located in the Ny phase or at Ny/PP interface. Low electrical resistivities were measured for the CB filled PP/Ny blends due to double percolation effect where CB is either located at the Ny/PP interface or within the Ny phase [Tchoudakov et al., 1996]. Zhang et al., [2004] used CB as filler in polypropylene(PP)/ethylene vinyl acetate (EVA) blend where the percolation threshold of the ternary CB/PP/EVA composites reached at 3.8 vol% of CB, while it was 7.8 vol% for the binary CB/PP composites without EVA. The conductivity of the ternary CB/PP/EVA composites was upto $10^{-2}$ S/cm when the CB percentage was 5 vol %, while that of the binary CB/PP was lower than $10^{-2}$ S/cm when the CB percentage was upto 10 vol%. The addition of CB and EVA resulted in decrease in crystallinity of the PP with the CB particles forming branches in the blend matrix [Zhang et al., 2004].

Thus, reduction of the percolation threshold and enhancement of electrical conductivity in insulating polymer matrix composites has been attempted by various methods. These methods were aimed at changing the structural properties of the
polymer matrix which in turn facilitated better self assembly of CB particles in the matrix and thus forming better conductive networks.

A novel approach towards this aim could be the use of a filler like FA which has the capability of changing the structural properties of the polymer matrix to facilitate self assembly of CB within the matrix and also impart electrical conductivity when present in the matrix in combination with CB. With this aim both CB and FA could be used as fillers in a recycled polymer system forming hybrid polymer composite.

1.12 Hybrid polymer composites: Literature review

Hybrid polymer composites are developed from the incorporation of “two fillers” in a polymer matrix. The ‘synergistic effect’ of both fillers in a composite has the ‘best of both worlds’ in them. Various combinations of fillers have been used in polymer matrices to achieve tailor made properties [Lee et al., 1996; Lee et al., 2006; Nayak et al., 2010]. Chand et al., [1994] used fly ash and glass fibre in unsaturated polyester resin composites to investigate the influence of load on the abrasive behaviour of the composites. Gupta et al., [2001] used fly ash as filler in combination with glass fibre filled composites and studied its effect on the compressive and impact properties of the resulting composites. Addition of fly ash particles lowered the compressive strength of the glass fibre reinforced composites.

The role of carboxy terminated poly (acrylonitrile-co-butadiene) (CTBN) and fly ash (as individual filler and also as mixed filler) in the epoxy resin matrix was investigated by Kishore and Santra [2005a, 2005b, 2005c] and they reported their compressive and impact properties. It was found that when CTBN or fly ashes were
used as reinforcement separately in the epoxy resin matrix, the highest compressive strength reached within 3–6 vol% of fillers. But when they together were used as hybrid reinforcement, the peak in compressive strength reached where the two fillers were present at 3.2 vol% level. In case of impact studies, it was reported that the energy absorbed was much higher for the CTBN/fly ash filled epoxy matrix composites compared to the individual filler bearing ones [Kishore and Santra, 2005a, 2005b, 2005c]. Dadkar et al., [2009] reported the incorporation of fly ash in combination with aramid fibres in phenolic based hybrid polymer matrix composites for use in friction braking applications. The friction-fade and friction-recovery behaviour were evaluated as a function of in situ braking induced temperature rise in the disc at the braking interface on a Krauss friction testing machine. The fade behaviour has been observed to be highly dependent on the weight fraction of resin i.e. followed by a consistent decrease with decrease in the fly ash content, whereas the frictional fluctuations was observed to decrease with the increase in fly ash content. A higher recovery response was registered when the fly ash content was 80 wt% [Dadkar et al., 2009]. Dadkar et al., [2010] investigated the use of fly ash and mineral rock (lapinus™) fibres in polymers for developing hybrid composite friction materials. The analysis of friction and wear performance revealed that fly ash along with lapinus fibre provided thermo-mechanical stability and overall mechanical integrity to the system causing reduction in friction-fade whereas wear was found to be more recovery-controlled and less fade controlled. Worn surface morphology investigation using Scanning electron microscopy (SEM) revealed that the interplay of fly ash–lapinus combination largely influenced the friction and wear performance of such composites [Dadkar et al., 2010].
Verma et al., [2012] investigated the use of fly ash and bagasse fibre reinforcement in epoxy composites. The hybrid composites showed better tensile properties than the single filler/polymer composite but the flexural and compressive strengths decreased.

Thongsang et al., [2012] studied the dynamic mechanical analysis and tribological properties of natural rubber (NR) filled with fly ash silica (FaSi) and precipitated silica (Psi) in 10:0, 75:25, 50:50, 25:75 and 0:100 ratio where mechanical properties were found to improve with increasing PSi content [Thongsang et al., 2012].

There has been a report on hybrid composites of CB and short carbon fibre in order to develop pressure-sensitive electrically conductive nitrile rubber composites. The synergistic effects of the fillers increased the electrical conductivity of the composites [Pramanik et al., 1990]. Ma et al., [2009] reported the reinforcement of epoxy resin with carbon nanotubes (CNT’s) and carbon black (CB). Varying combination of CNT’s and CB as conducting fillers and their influence on electrical and mechanical properties were evaluated. It was shown that the addition of CNT’s in CB composites enhanced the electrical conductivity of composites by achieving a low percolation threshold with 0.2 wt% CNT’s and 0.2 wt% CB particles. The CB particles also enhanced the ductility and fracture toughness of the nanocomposites. Thus synergistic effect of the two fillers CB and CNT with unique geometric shapes and aspect ratios were observed [Ma et al., 2009]. Etika et al., [2009] studied the influence of synergistic stabilization of carbon black (CB) and clay on the electrical and mechanical properties of epoxy composites. This unique microstructural development increased the electrical conductivity on addition of 0.5 wt% clay by an order of magnitude (relative to composites containing no clay), but there was no increase in the storage modulus values. Composites with equal concentrations of CB and clay showed reduced electrical conductivity but higher storage modulus. In
composites containing 1: 2 clay: CB ratio, both electrical conductivity and storage modulus were found to increase [Etika et al., 2009]. CB, the primary filler in natural rubber compounds, has been used in combination with bagasse fibre ash (75% silicon dioxide) to alter the mechanical properties of the composites. In the hybrid filler system, BFA could be used in combination with CB in the ratio BFA: CB:: 3:1 up to which it does not affect the ultimate mechanical properties of the composites [Kanking et al., 2012].

Both fly ash and carbon black have been used in various combinations with different fillers to achieve multiple functions. But they have never been studied together. In this study both fly ash and carbon black will be used as ‘hybrid filler’ in recycled polymer (polyethylene) composites.
1.13 Summary and Scope of the work

The objective of this work was to develop sustainable, value-added polymer composites from waste based precursors having various engineering applications. Fly ash, the industrial waste, has been used as the principal filler in the recycled polymer matrix composites aiming at its maximum utilization.

The work is divided in two parts.

- Incorporation of surface coated fly ash in recycled polypropylene (R) matrix composites. Fly ash and polypropylene have been used in 1:1 weight ratio in order to achieve maximum uptake of the filler. The interfacial interaction between the filler and the matrix has been achieved by using green, unconventional coupling agents like lauric, palmitic, stearic acid and an ester of palmitic acid, furfuryl palmitate. Each coupling agent has been used in 1, 2, 3 and 5 wt % with respect to the FA weight.

- Incorporation of fly ash and carbon black (CB) filler in recycled polyethylene (RP) matrix to form hybrid multifunctional composites. The filler fly ash has been used in 1:19, 1:3 and 1:1 ratio in the RP matrix and CB has been added in 5, 8 and 10 wt% w.r.t to the composite where FA/RP has been considered as the matrix.

Distinct effect of the presence of the fillers and coupling agents were witnessed in the polymer composites. Incorporation of surface coated fly ashes was aimed at achieving enhanced mechanical and thermal properties and to ensure changes in the structural properties of the recycled polymer matrix composites.
Both fly ashes and carbon black were used as hybrid fillers in the recycled polyethylene matrix composites in order to evaluate the role of both the fillers in enhancing the electrical properties of such composites. This could be achieved by lowering the percolation threshold of CB and increasing the electrical conductivity in presence of both CB and FA.

This thesis is divided in 8 chapters:

**Chapter 2:** It contains the detailed description of the experimental procedure, such as

- Materials and methods including the characteristics of fly ash used and surface coating of the fly ash particles.
- Fabrication of surface coated fly ash filled recycled polypropylene composites and
- Fabrication of fly ash and carbon black filled recycled polyethylene based hybrid composites.
- It also contains the characterisation details including instruments, test procedures etc.

**Chapter 3:** It involves the study of lauric acid (12C chain) coated fly ash filled recycled polypropylene matrix composites.

**Chapter 4:** It involves the study of palmitic acid (16C chain) coated fly ash filled recycled polypropylene matrix composites.

**Chapter 5:** It involves the study of stearic acid (18C chain) coated fly ash filled recycled polypropylene matrix composites.
Chapter 6: It involves the study of furfuryl palmitate coated fly ash filled recycled polypropylene matrix composites.

Chapter 7: It involves the study of the fly ash and carbon black reinforced recycled polyethylene based hybrid composites.

Chapter 8: General Conclusions.
This chapter deals with the details of the materials used in this study, procedures for fabrication of the polymer composites and details of the composition of all the composites. It also contains the information on the characterization techniques used along with the details of the instruments operated and the test parameters used in this study.