2. LITERATURE REVIEW

Natural fibres have attracted the interest recently due to their abundance in nature, low cost, biodegradability and enormous advantages over synthetic fibres. Synthetic fibres such as carbon, nylon, glass, and aramids have been widely used for number of applications for more than two decades. The synthetic fibres have number of disadvantages, especially regarding the environment and their handling. Effective utilization of natural fibres, derived from a number of renewable resources, as reinforcing material in polymer matrix based composite materials are replacing synthetic fibres in various fields and providing positive environmental benefits.

Natural fibres have certain disadvantages like moisture absorption, quality variations, low thermal stability and poor compatibility with hydrophobic polymer matrix. Various chemical modifications and treatments such as graft copolymerization, mercerization, silane treatment, peroxide treatment, acetylation, benzoylation, permanganate treatment etc. have been used to overcome the disadvantages associated with natural fibres. Chemical modifications may activate the hydroxyl groups or introduce new moieties that can effectively interlock with the cellulose and induce required properties in the polymer. As a result, considerable efforts have been made toward improving the quality of the interfacial bonding between the polymer and fibres by surface modification of natural fibres (Khullar et al., 2007).

Graft copolymerization is a commonly used method for the surface modification of natural fibres. It modifies the physical, chemical and mechanical properties of natural fibres (Thakur and Singha, 2014). Graft copolymerization of vinyl monomers onto natural fibres has advantages of adding properties of the monomer without destroying its basic properties. Graft copolymerization of different vinyl monomers has been successfully attempted onto both natural and synthetic polymers such as natural fibres, starch, chitosan, gelatine, nylon poly(vinyl alcohol) etc. A considerable number of studies on the graft copolymerization of monomers onto natural fibre using different initiator system have been recorded. The grafting onto natural cellulosic
fibres provides an opportunity to prepare tailor made material for specific applications. Grafting through microwave radiation technique is another effective method in terms of time consumption and cost effectiveness (Tsukada et al., 2005).

The chemically modified natural fibres have gained the properties such as hydrophobic and hydrophilic character, heat resistant, resistance to microbial attack, thermosensitivity, pH sensitivity, and potential adsorbent for hazardous dyes removal, sorption, fabrication of drug delivery system, removal of metal ions and as reinforcing material for thermoplastic, thermosetting and biodegradable polymer composites.

2.1. GRAFT COPOLYMERIZATION

The history of polymer modification by copolymerization began around 1910 when it was discovered that copolymers of olefins and dienes resulted in better elastomers than polyolefins or polydiens alone. In 1943, first graft copolymer of vinyl and allyl ethers of cellulose copolymerized with maleic acid ester was reported (Ushakov, 1943). The concept of graft copolymer was actively promoted by Mark in 1953. During last decades several methods have been suggested for the preparation of graft copolymers by conventional chemical techniques.

Graft copolymerization of different vinyl monomers has been successfully attempted onto both natural and synthetic polymers. Graft copolymerization of vinyl monomer onto polymeric materials has been the subject of extensive studies for about four decades due to its abundance in nature. The physicochemical properties such as chemical resistance, moisture absorption, water uptake behaviour etc., of natural fibres (jute, hemp, flax, ramie, sisal, pinus, oil palm, coir, bamboo, okra, agave, Grewia optiva, Cannabis indica, Hibiscus sabdriffa etc.) have been improved by graft copolymerization (Singha and Rana, 2012).

Initiator plays an important role on the grafting, and determines the grafting percentage. The grafting of vinyl monomers onto cellulose or cellulose derivatives
was performed by chemical initiators. Redox initiator systems can be used at low temperatures, and they react only with the amorphous region of cellulose because the latter are more reactive than the crystalline phase. The redox initiators such as ceric (IV) ion (ceric ammonium nitrate (CAN) or cerium (IV) sulfate (Okieimen and Ebhoaye 1986; Bical et al., 1999; Gupta and Khendekar, 2002), ceric ammonium sulfate (CAS) (Ibrahim et al., 2002), iron(II)-hydrogen peroxide (Fe$^{2+}$-H$_2$O$_2$:Fenton reagent) (Fanta et al., 1987), cobalt (III) acetylacetonate complex salts (Gupta and Sahoo, 2001), Co(II) potassium monopersulfate (Sahoo et al., 1986), and sodium sulphite-ammonium persulfate (Yang et al., 2009) have been attempted for the grafting of different vinyl monomers onto the cellulosic fibres. The free radical initiators such as azobisisobutyronitrile (C$_8$H$_{12}$N$_4$: AIBN) (Oiajai et al., 2004), potassium persulfate (K$_2$S$_2$O$_8$: KPS) (Abdel, 1997; Abdal, 1990; Bardhan, 1997; Ibrahim, 2008; Liu and Sun, 2008; Mukhopadhyay, 1975), ammonium persulfate ((NH$_4$)$_2$S$_2$O$_8$: APS), and benzoyl peroxide (C$_{14}$H$_{10}$O$_4$: BPO) have also been used for the grafting of different monomer onto natural fibres.

Potassium bromated thiourea redox system was used for initiation of graft copolymerization of methyl methacrylate (MMA) onto nylon-66 (Habeish et al., 1976). The grafting of acrylamide (AAm) or acrylonitrile (AN) onto nylon 6 or nylon-66 to produce N-grafted polyamides via redox reaction was investigated (Kein et al., 1979). Lui et al. (2002) have used the potassium diperiodatonickelate [Ni(IV)]-casein, novel redox system to initiate the graft copolymerization of butyl acrylate (BA) onto casein under heterogeneous conditions in aqueous medium.

Lenka et al. (1982) carried out the graft copolymerization of MMA onto nylon-6 using acetyl acetonate complex of Mn(III), Co(III) and Fe(III) as initiators. It was observed that the rate of polymerization, increased with increase in concentration of initiators in the initial stages and decreased with further increase of complex concentrations. Graft copolymerization of acrylonitrile (AN) onto pineapple leaf fibre (PALF) was studied using CuSO$_4$ and KIO$_4$ combination as an initiator in an aqueous medium. The thermal stability of grafted samples was recorded higher (Mohanty et
The grafting of binary mixture of acrylonitrile and methylacrylate onto cellulosic fibres was carried out in the presence of Ce(IV) ions. It was observed that the extent of grafting changes appreciably on varying the comonomers concentration (Gupta and Sahoo, 2000; Meng et al., 2009).

The grafting of vinyl monomers onto natural fibres was also performed by radiation or microwave irradiation. The use of microwave irradiation to induce multicomponent polymerization reactions is a new area of increasing interest. The use of microwave irradiation was used to reduce reaction times as compared to traditional thermal initiated reactions. Kaith et al. (2007) has investigated the improvement in chemical resistant behaviour of methylmethacrylate (MMA) grafted flax fibre under the influence of microwave radiation (MWR).

Singha and Rana (2012) investigated the improved swelling behaviour of natural Cannabis indica fibre from graft copolymerization of acrylic acid onto by using CAN/nitric acid redox initiator system under the influence of microwave radiation (MWR). Grafting of methyl methacrylate (MMA) onto delignified Grewia optiva fibre using ascorbic acid/H₂O₂ as an initiator was carried out under microwave irradiation (Singha et al., 2014). The corn starch was grafted with acrylic acid using potassium persulphate (KPS) as redox initiator by microwave irradiation. It has been observed that the molecular chains of corn starch were introduced to hydrophilic and hydrophobic groups (Wai et al., 2011).

Gamma irradiation induced graft copolymerisation of acrylonitrile onto cellulosic filter paper has been reported. It has been observed that the amount of homopolymer was reduced by the introduction of a small amount of styrene monomer (Badawy et al., 2001). Glycidyl methacrylate (GMA) has been grafted onto Kapok fibre under irradiation with 60Co gamma rays. It has been observed that graft polymerization of GMA onto polymer substrates was used as ion exchangers and adsorption of toxic gas (Kang et al., 2007).
The monomers such as acrylic acid (AA), acrylamide (AAm), 2-acrylamidomethylpropane sulfonic acid (AASO₃H), etc., have been grafted onto cellulose to obtain a cellulose graft copolymer with high water or moisture absorbency and hydrophilic character. The compatibility and adhesion of cellulosic fibres with hydrophobic composites have been enhanced by grafting of hydrophobic monomers such as methyl methacrylate, styrene, acrylonitrile, butadiene, isobutyl vinyl ether, and vinyl acetate.

Rute et al. (2002) have studied the improved hydrophobicity and mechanical strength of coir fibres thorough AN grafting using CuSO₄/NaIO₄ system as the initiator in an aqueous medium. Physico-chemical properties have improved by graft copolymerization of butyl acrylate (BA) onto oil palm empty fruit bunch fibre (OPEFB) using H₂O₂/Fe²⁺ as a redox initiator in aqueous solution (Ibharim et al., 2003) Graft copolymerization of ethyl acrylate (EA) onto water soluble hydroxypropyl methylcellulose (HPMC) has been investigated by using potassium persulfate (KPS) as initiator in an aqueous medium. The decrease in the humidity, absorption was recorded for grafted samples (Wang and Xu, 2006).

Kumar et al. (2006) reported the preparation of an anion exchange matrix, poly(vinyl benzyltrimethyl ammonium chloride)-g-cotton cellulose, using ⁶⁰Co gamma-radiation source. The resultant material exhibited excellent protein adsorption properties. The hyper branched aliphatic polyester grafted from the surface hydroxyl groups of natural cotton fibres via the solution polycondensation of 2, 2-bis(hydroxymethyl) propionic acid (bis-MPA) using p-toluenesulfonic acid (p-TSA) was investigated. It was used for the removal of heavy metal ions from waste water (Liu, 2007; Nada et al., 2007; Ye et al., 2010).

Several workers have studied the graft copolymerization of binary vinyl monomer mixtures onto cellulosic fibres. Grafting of flax fibre with binary vinyl monomer mixtures such as methyl methacrylate (MMA)-ethyl acrylate (EA), MMA-acrylonitrile (AN), and MMA-acrylic acid (AA) has been studied to improve the...
thermal stability of the fibre (Kaith and Kalia, 2007; Mittal et al., 2010). Thermal stability and crystalline behaviour of sunn hemp fibres (SHF) modified with ethyl acrylate and binary monomers (EA+MMA, EA+AA) thorough microwave radiations induced graft copolymerization have been investigated (Kalia et al., 2011).

Ojah et al. (2006) investigated the thermal stability of methyl methacrylate (MMA) grafted Bombyx mori fibre (natural silk). The graft copolymerization was carried out by photopolymerization of MMA using semiconductor particles as photocatalyst in the presence of visible light. Khullar et al. (2007) have studied the graft copolymerization of acrylonitrile (AN) onto cellulosic material derived from bamboo (Dendrocalamus strictus) in heterogenous medium, initiated with ceric ammonium nitrate (CAN). It has been observed that the hydrophobic nature was higher for grafting samples.

Khan et al. (2007) have studied the graft copolymerization of acrylic acid onto bleached jute fibre in aqueous solution using redox initiation system (K₂S₂O₈/FeSO₄). The grafted fibre depicted greater tensile strength as compared of bleached fibre. Textile strength of okra bleached fibres was improved by grafting of acrylonitrile (AN) using potassium persulphate as redox initiator (Khan et al., 2009). Kinetics of graft copolymerization of acrylic acid onto Cannabis indica fibre has been reported by Singha and Rana (2011).

The improvement in water uptake and moisture absorbance properties were observed in methyl methacrylate (MMA) grafted mercerized flax fibres (Kaith and Kalia, 2008). The enhancement in mechanical properties of MFx-g-MMA and Flax-g-poly(MMA-co-AAm) fibres reinforced polystyrene matrix based composites has been observed (Kaith et al., 2008; Kalia et al., 2009; Kalia and Kaith, 2009). Surface modification of natural fibres using graft copolymerization improved the swelling behaviour, water uptake, moisture absorbance, resistance to chemicals, and thermal behaviour (Singha and Rana, 2010).
Graft polymerization of polyacrylonitrile (PAN) onto cellulosic material obtained from rubber (*Hevea brasiliensis*) seed shell using ceric ammonium nitrate (CAN) as initiator was investigated. The grafted product was used for the sorption of different metal ions such as Cr, Mn, Ni, Cu, and Pb from water system (Ekebafe *et al*., 2010; Chauhan *et al*., 2010).

Pathania *et al*. (2011) investigated the graft copolymerization of methacrylic acid (MAA) onto cellulosic fibre derived from *Luffa cylindrica* using chromic acid as initiator. The percent crystallinity of grafted fibres was found to be higher as compared to ungrafted fibre.

Graft copolymerization of methyl acrylate (MA) monomer onto *Saccharum cilliare* fibres has been attempted. The grafting reduced the affinity of cellulosic fibres toward water and improved the swelling behaviour in different solvents and chemical resistance (Thakur *et al*., 2012).

The free radical polymerization of different monomers such as MMA and EA using CAN/HNO₃ as initiator was attempted on *Hibiscus sabdariffa* and *Saccharum cilliare* fibres, respectively (Thakur *et al*., 2012; Thakur *et al*., 2013). It has been observed that the thermal and physicochemical properties of grafted fibres were found to be more as compared to ungrafted fibres. The Mechanical properties, physicochemical properties and kinetics of graft copolymerized *Grewia optiva* has been investigated (Singha and Rana, 2012; Priya *et al*., 2014).

Singha *et al*. (2013) have successfully revealed the kinetics of graft copolymerization of methyl methacrylate (MMA) onto *Abelmoschus esculentus* fibres in aqueous medium using ascorbic acid and hydrogen peroxide as redox initiator. The grafted fibres with improved thermal properties, hydrophobicity, chemical resistance, moisture absorbance and swelling behaviour have been potentially used as reinforcement for thermosetting, thermoplastic and biodegradable polymer composites.
2.2. CHEMICAL MODIFICATION OF NATURAL FIBRES

The interest in using natural fibres for the preparation of composites has increased in recent years due to their lightweight, nonabrasive, combustible, nontoxic, low cost and biodegradable properties. Hydrophilic nature of natural fibres reduces their potential as reinforcing agents due to the low interfacial properties between fibre and polymer matrix. However, lack of good interfacial adhesion, low melting point and poor resistance to moisture absorption, make the use of natural fibre reinforced composites less attractive. The pre treatments of the fibre clean the fibre surface, chemically modify the surface, stop the moisture absorption process, increase the surface roughness and improve the fibre matrix interaction. The chemicals may activate hydroxyl groups or introduce new moieties that can effectively interlock with the matrix. Many chemical treatments such as mercerization, isocyanate treatment, permanganate treatment, acetylation, silane treatment and peroxide treatment with various coupling agents etc., have been attempted for the modification of fibre surface and enhance its properties (Thakur et al., 2012).

2.2.1. Mercerization

Alkaline treatment causes the disruption of hydrogen bonding in the network structure due to which surface roughness increases. This treatment removes the lignin, wax and oils from the fibre cell wall. Moreover, mercerization increases the number of possible reactive sites and allows better fibre wetting. Garcia et al. (1998) reported that 2% alkali solution at 200°C and 1.5 MPa pressure for 90 seconds was suitable for degumming and defibrillation to individual fibres. Sreekala et al. (2000) indicated that the 10-30% sodium hydroxide (NaOH) solution produced the best effects on flax fibre properties. Flax fibres soaked in different solution of NaOH (2.5, 5, 10, 13, 15, 18, 20, 25, or 30%) were studied for the surface modification. It has been found that 5 and 18% of sodium hydroxide solution were the appropriate concentrations for mercerization of the flax fibres.
Jute fibres were treated with 5% alkali solution for 0, 2, 4, 6, and 8 hour at 30°C (Ray et al., 2001). Mishra et al. (2003) reported that 5% NaOH treated sisal fibre-reinforced polyester composite had better tensile strength than 10% NaOH treated composites. Van de Weyenberg et al. (2003) reported that alkali treated flax fibre was used as reinforcement in epoxy resins. It was observed that alkaline treatment increased about 30% tensile properties (both strength and modulus) of flax fibre-epoxy composites. Jacob et al. (2004) examined the effect of NaOH concentration (0.5, 1, 2, 4 and 10%) for treatment of sisal fibre reinforced composites and concluded that maximum tensile was observed for 4% NaOH treatment.

2.2.3. Benzoylation

Benzoyl chloride is most often used for the benzoylation treatment of the fibre. It improves the fibre matrix adhesion which considerably increases the strength of composite. Benzoylation decreases the water absorption. It also improves the thermal stability of natural fibre. Joseph et al. (2000) used the NaOH and benzoyl chloride (C₆H₅COCl) solution for surface treatment of sisal fibres. Nair et al. (2001) postulated a hypothetical model of the interface of benzoylated sisal fibre composite. It was observed that the thermal stability of treated composites were higher than the untreated fibre composites.

Benzoylation of Cannabis indica fibre was carried out by treating raw fibre with varying concentrations (1, 2 3, 5, 7 and 9%) of benzoyl chloride solution. The chemical resistance and hydrophobic behaviour of surface modified Cannabis indica fibres was increased (Singha and Rana, 2012). Wang, 2004 treated the flax fibres with NaOH to activate the hydroxyl groups. It has been observed that the interfacial adhesion of benzoylated flax fibre and polyethylene (PE) matrix was improved after treatment.

2.2.4. Silane treatment

Treatment of natural fibres with silane solutions in a water and ethanol mixture with concentration between 0.033% and 1% was investigated by Valadez et al. (1999).
Agrawal et al. (2000) have used the aminopropyl trimethoxy silane to modify the surface of henequen fibres and oil palm fibres. Flax fibre surface was modified by using aminopropyl trimethoxy silane with concentration of 1% in a solution of acetone and water (50/50 by volume) for 2 hours (Weyenberg et al., 2003).

Rong et al. (2001) have modified the sisal fibre surface by soaking in a solution of 2% aminosilane and 95% alcohol for 5 minutes at 4.5-5.5 pH value. The silane treated fibres were used as reinforcement for the preparation of thermosetting composites. Singha and Rana (2009) have reported the silane treatment of *Grewia optiva* fibres with aminopropyl triethoxy silane as a coupling agent for the improvement of the physic-chemical properties of raw fibre after silane treatment. Silane treated *Grewia optiva* fibres were reinforced in urea formaldehyde resin to improve the mechanical and thermal properties.

### 2.2.5. Acetylation

Acetylation is beneficial for reducing the moisture absorption of natural fibres. Bledzki and Gassan, in 1999, reported the 50 and 65% moisture uptake for acetylated jute and acetylated pine fibres, respectively. Acetylated fibres have use as reinforcement material for the preparation of biocomposites (Paul et al., 1997; Rong et al., 2001; Sreekala and Thomas, 2003). Nair et al. (2001) have attempted the acetylation of sisal fibre in 18% NaOH solution, acetic acid, acetic anhydride and sulphuric acid for 1 hour.

Mishra et al. (2003) studied the acetylation of dewaxed sisal fibres. The decrease in the moisture absorption was observed for the treated fibres. Acetylated flax fibre reinforced polypropylene composite were prepared by Bledzki et al. (2008). It was observed that the flax fibre surface morphology and moisture resistance properties improved remarkably after acetylation treatment. Tensile and flexural strengths of acetylated flax fibre reinforced polypropylene composite were found to increase as compared to untreated flax fibre reinforced composite.
2.2.6. Isocynate treatment

Joseph and Thomas (1996) studied the chemical treatment of sisal fibres with cardanol derivative of toluene-di-isocyanate (CTDIC) as coupling agent. The treated sisal fibres were used as reinforcement materials in LDPE matrix based composites. Pineapple leaf fibres were treated with polymethylene-polyphenyl-isocyanate (C\textsubscript{15}H\textsubscript{10}N\textsubscript{2}O\textsubscript{2}) solution at 50°C for 30 minutes to improve the fibre-matrix interfacial adhesion (George et al., 1996). Wu et al. (1996) investigated the grafting of isocyanate terminated elastomers onto the surfaces of carbon fibres (CF). Sreekala et al. (2000) investigated that the TDIC treated oil palm fibre were reinforced in phenol formaldehyde matrix. It was observed that the tensile strength of treated composites was higher than untreated fibre reinforced composites.

2.2.7. Sodium chlorite treatment

Sodium chlorite (NaClO\textsubscript{2}) is usually used for bleaching the fibres. It also delignify the lignocellulosic fibres. Flax fibres were treated with sodium chlorite for the surface modification (Mustata et al., 1997). Mishra et al. (2002) have been investigated the treatment of sisal fibre in sodium chlorite with a liquor ratio of 25:1 at 75°C for 2 hours. Tensile strength of bleached sisal fibre-phenol formaldehyde composite was found less than other chemical treated fibre composites. It may be due to the fact that the delignification of the fibre lowered the tensile strength of the fibres. Textile strength of okra bleached fibres has improved by grafting acrylonitrile (AN) using potassium persulphate as redox initiator (Khan et al., 2009).

Jonoobi et al. (2009) have investigated the thermal resistance and crystalline structure of Kenaf fibre (Hibiscus cannabinus) fibre. Rich cellulose content was found in sugarcane bagasse after treating it with sodium chlorite (Pereira et al. 2011). Green coconut fruit fibres were treated with alkaline solution and bleached with sodium chlorite. Bleached fibres were used as reinforcement in high impact polystyrene. It was observed that the tensile strength of treated composites was higher than that of untreated fibre reinforced composites.
2.2.8. Maleated coupling agents

Maleated coupling agents are widely used to strengthen the composites containing fillers and fibre reinforcements. Banana, hemp and sisal fibres were treated with maleic anhydride. Treated fibres were used as reinforcement materials for fibre-reinforced novolac composites. Treated fibres reduced the water absorption of the composites. Mechanical properties like young’s modulus, flexural modulus, hardness and impact strength of fibre reinforced composites were increased after maleic anhydride treatment (Mishra et al., 2000).

Mohanty et al. (2004) used the maleic anhydride grafted polypropylene (MAPP) as coupling agent for the surface modification of jute fibres. Different parameters such as time, fibre loading, MAPP concentration and fibre length were optimized to obtain the maximum tensile strength. It has been found that 30% fibre loading with 0.5% MAPP concentration in toluene with 6 mm average fibre lengths showed 72.3% of flexural strength.

2.2.9. Permanganate treatment

Permanganate treatment was attempted by using different concentration of potassium permanganate (KMnO₄) solution in acetone after alkaline pretreatment (Joseph and Thomas 1996; Shreekala et al., 2000; Shreekala et al., 2002). Sisal fibres were modified by dipping in permanganate solution of concentrations (0.033, 0.0625 and 0.125%) (Paul et al., 1997). The decrease in hydrophilic tendency of fibres was studied after treatment. The water absorption of fibre-reinforced composite decreased. The hydrophilic tendency of fibre decreased with increased concentration of KMnO₄.

2.2.10. Peroxide treatment

Natural fibres were modified using alkali and benzoyl peroxide solution of different concentration at different time intervals. Treated fibres were found to be thermally stable and showed enhanced crystallinity (Kaushik et al., 2012). Peroxide treatment of fibre was performed by using 6% benzoyl peroxide or dicumyl peroxide in acetone
solution for about 30 minutes after alkali pre-treatment. Sisal fibres treated with peroxide were used as reinforcement material in low-density polyethylene. Tensile and electrical properties of composites were found higher (Paul et al., 1997). Peroxide treated oil palm fibres were reinforced in phenol formaldehyde resin. It has been observed that treated fibre reinforced composites were hydrophobic in nature (Sreekala et al., 2000; Sreekala et al., 2002). Flax fibres were treated with dicumyl peroxide after alkali pre treatments (Wang et al., 2007).

### 2.3. NATURAL FIBRE REINFORCED COMPOSITE

Several bio based fibres such as wood, sisal, jute, flax, abaca, banana, oil palm, pineapple leaf, bamboo etc. have been studied as reinforcements for the preparation of composites. Natural fibres in composites materials act as load carrying material (reinforcement) imbedded in matrix. Reinforcement provides strength and rigidity, helping to support the structural load. The matrix or binder (organic or inorganic) maintains the position and orientation of the reinforcement. The constituents of the composites retain their individual, physical and chemical properties.

In the past decade mechanical properties, processing technologies and the interfacial compatibility of cellulose fibre reinforced composites were investigated extensively. Use of natural fibres as reinforcement in thermoplastics and thermosetting matrix has a number of technological and environmental benefits.

Natural fibre reinforced composites have been used in various fields such as aerospace, automotive, marine, infrastructure, military, etc. Natural fibres have certain advantages over traditional reinforcing materials such as synthetic fibres (glass fibre, carbon fibre, etc.) Natural fibre reinforced composite have specific properties such as easy availability, light weight, ease of separation, enhanced energy recovery, high toughness, non-corrosive nature, low density, low cost, good thermal properties, reduced tool wear, and respiratory irritation, cause less abrasion to processing equipment, renewability and minimize the environmental pollution. The tensile
properties of composites have been improved by adding fibres to a polymer matrix. The mechanical properties such as elastic modulus and ductility of biocomposites increased substantially as compared to the neat polymers matrix. The mechanical properties of most of fibre reinforced composites increased with the increase in the amount of fibre in the polymer matrix. The fire performance of composite material has been improved by using additive type fire retardants. Additive type flame retardants are added to the composite material during processing. Flame retardants are present in many forms, although most suitable are particles or powders (Deo et al., 2008).

Fibre reinforced composite materials not only act as effective insulators, but also provide mechanical support for field carrying conductors. Composite materials are increasingly used for dielectric applications. The electrical applications of composite materials have been determined in terms of dielectric constant, volume resistivity and loss factor.

The composite materials find extensive applications in different areas, like in electrical industry as electrical insulation, encapsulation, multilayer ceramic chip and capacitors and for piezoelectric, ferroelectric, and pyroelectric devices that provide sensing, actuation, terminals, connectors, industrials and household plugs, switches, printed circuit boards etc. The incorporation of fibre to the polymer matrices is suitable for electrical applications.

Jayamol et al. (1997) have investigated the electric properties of pineapple reinforced polyethylene composites. The increase in the dielectric constant of composite with fibre loading was due to increased orientation and interfacial polarization of cellulosic fibre.

Thwe and Liao (2003) have studied the durability of bamboo fibre reinforced in polypropylene polymer matrix. The improvement in properties such as tensile strength and elastic modulus of bamboo fibre was observed. Rice husk was reinforced with polypropylene matrix and the flame retarding effect was studied (Sain et al.,
2004; Deo et al., 2008). It was observed that magnesium hydroxide increased the flame retardancy of composites.

Joseph and Thomas (2008) have investigated the electric properties of banana fibre and glass fibres reinforced phenol formaldehyde matrix. It has been observed that banana fibre reinforced phenol formaldehyde composite showed good electric properties as compared to treated and glass fibres.

Arbelaiz et al. (2005) have studied the mechanical properties of flax fibre reinforced polypropylene composites. It was reported that the tensile strength and modulus of fibre reinforced composites depend on the fibre and matrix ratio.

Jute fibre reinforced polypropylene matrix composites have been developed by hot compression molding technique by varying parameters, such as fibre condition (untreated and alkali treated), fibre sizes (1, 2 and 4 mm) and percentages (5%, 10% and 15% by weight). The improvement in mechanical properties was observed with alkali treated fibres loading of 10% (Rashed et al., 2006).

The water absorption and dielectric behaviour of polyester matrix composite of glass and jute fibre was investigated. The dielectric constant of jute fibre reinforced composite was found to be higher than glass fibre due of higher water uptake (Fraga et al., 2006). Panthapulakkal and Sain (2007) reported the mechanical and thermal properties of hemp and glass fibre reinforced polypropylene (PP) composite materials. It was observed that the hybrid composite material enhanced the flexural and impact properties.

The addition of glass fibre into hemp-PP composites resulted in improved thermal properties as well as the water resistance. The tensile strengths of hardwood fibres reinforced with high density polyethylene (HDPE) composites increased gradually with fibre loading and reached to maximum at 25% (Facca et al., 2007).

Singha and Thakur (2008) have synthesised the urea formaldehyde matrix reinforced with Hibiscus Sabdariffa fibres. Mechanical properties such as tensile strength,
compressive strength, flexural strength, and wear resistance of the natural fibre reinforced composite increased with fibre loading.

Li et al. (2009) reported the flax fibres (10% to 30% by mass) reinforced in high-density polyethylene (HDPE) by extrusion and injection moulding to produce biocomposites. The results showed that increasing fibre content resulted in increased tensile properties. Kalia and Kaith (2008) synthesized the flax-g-copolymers reinforced phenol formaldehyde composites. The mechanical properties such as wear resistance, modulus of rupture (MOR), modulus of elasticity (MOE) and stress at the limit of proportionality (SP) were enhanced. The mechanical properties of microwave induced flax-g-copolymers reinforced composite was compared with flax-g-copolymer reinforced composites.

Saleem et al. (2008) investigated the effect of pectinase treatment on hemp (Cannabis sativa L.) fibres and studied their properties with polypropylene matrix based composites. The improved tensile and flexural property of these thermoplastic composites was recorded after treatment. The effect of hemp fibre content has been examined on the basis of tensile properties of the composite materials (Hajnalka et al., 2008). Khoathane et al. (2008) have reported the mechanical properties of bleached hemp fibre reinforced with 1-pentene-polypropylene (PP1) composite. The increase in the amount of hemp fibre resulted in the increase in the tensile strength of the composite. Mechanical and thermal properties of hemp fibres reinforced with polypropylene matrix were enhanced with the fibre loading (Kechaou et al., 2010).

Sisal fibres reinforced polypropylene composites of different weight percent sisal fibre with or without maleic anhydride have been developed. Mechanical and dielectric properties of composites with and without MA-g-PP have been determined. The improvement in the mechanical and dielectric properties of composites was observed (Chand et al., 2008).

Saccharum cilliare and Grewia optiva fibre have been reinforced with urea formaldehyde resin. Mechanical properties such as tensile strength, compressive
strength and wear resistance of urea formaldehyde composite was found higher. It has been observed that the particle reinforcement was more effective as compared to short and long fibre reinforcement (Singha and Thakur, 2009a; Singha and Thakur, 2009b).

Long discontinuous natural fibres of kenaf and jute have been reinforced in polypropylene (PP) matrix with fibre weight fraction varying from 10% to 70% (Lee et al., 2009). It has been observed that the tensile and modulus strength of both kenaf and jute fibre reinforced PP composites increased with fibre loading and found maximum at 30%.

Oxygen index and cone calorimeter tests has been used to characterize the fire performance of wood polyethylene composites, and compared with the unfilled polyethylene and solid wood. Fire retardent such as magnesium hydroxide and ammonium polyphosphate improved the fire performance of wood polyethylene composites (Stark et al., 2010).

Singha et al. (2011) have synthesized the Cannabis indica fibre reinforced composites. The Tensile properties of polyhydroxybutyrate (PHB) matrix and composite reinforced with sunn hemp (SH) fibre have been found to be 56 and 199 MPa, respectively. In case of fibre reinforcement with SH-g-poly(EA), SH-g-ploy(EA+MMA), SH-g-poly(EA+AA), the tensile strength of composites was found to be 315, 318, and 295 MPa, respectively (Kalia et al., 2011). Mechanical properties such as tensile strength (TS), bending strength (BS) and bending elongation (BE) of jute fibre reinforced low density polyethylene (LDPE) composites prepared by compression moulding of (10-30% fibre, by weight) was found more as compare to LDPE (Miah et al., 2011).

Flame retardancy of urea formaldehyde (UF) board made from saw dust fibres has been investigated. Flame retardant chemicals such as boric acid (BA) and borax (BX) were incorporated with saw dust fibres. It has been observed that the highest concentration of BA+BX enhanced the fire retardancy of composites (Nagieb et al., 2011). Sisal-jute-glass fibre reinforced polyester composites was developed and their
mechanical properties such as tensile strength, flexural strength and impact strength was evaluated (Ramesh et al., 2013). It was observed that the incorporation of sisal-jute fibre with glass-fibre reinforced polymers (GFRP) improved the mechanical properties and used as an alternate material for glass fibre reinforced polymer composites.

Brown grass flower broom fibre reinforced epoxy composites have been prepared (Dhal and Mishra, 2013). The dielectric properties (relative permittivity and loss factor) of pure epoxy resin and composites with different amount of broom fibre-reinforced polymer composite have been studied in the frequency range from 100 MHz to 1 MHz. The results indicated that the dielectric constant and dielectric loss factor decreased with frequency. It may be due to the orientation polarization. The increase in temperature was due to greater movement of polar molecular dipole which appears to be beneficial in electronic industry.

2.4. BIODEGRADABLE POLYMER COMPOSITES

Biodegradable polymers have been stimulated and developed to overcome problems regarding the persistence of plastic wastes in the environment. Biodegradable materials and composites have been used in different fields such as packaging, paper coating and other disposable articles, as well as in biomedical applications such as restorable surgical sutures, implants and controlled drug delivery devices.

Soyparotein resins were blended with ramie fibres to obtain composites. The soyprotein was mixed with starch and glycerol in the presence of sodium sulphite and extruded to form pellets. The composites showed good mechanical properties (Otaigbe et al., 1999). Bahourami et al. (2003) have synthesized the poly(vinyl alcohol)-chitosan blend films using glutaraldehyde as a crosslinking agent. It has been observed that crosslinker improved the tensile strength and decreased the elongation of the films. PVA content in the blends increased the water uptake while cross-linking with glutaraldehyde decrease the hydrophilicity.
Katori and Kimura (2002) and Lee et al. (2005) have synthesized the silk/poly(butylenes succinate) (PBS) biocomposites. It was found that the manufacturing processes effects the mechanical properties including tensile strength, fracture toughness and impact resistance, and thermal stability of biocomposites. Polyols (glycerol, sorbitol, and manitol) were used as a plasticizer to improve the rheological and thermal properties of zein resin films (Ghanbarzadeh et al., 2006).

Lee and Wang (2006) have investigated the effects of lysine based diisocyanate (LDI) coupling agent on the properties of biocomposite of bamboo fibre (BF) reinforced poly(lactic acid) (PLA) and poly(butylene succinate) (PBS). It was observed that tensile properties, water resistance, and interfacial adhesion of both PLA/BF and PBS/BF composites were improved. Crystallization temperature and enthalpy of the composites were increased with increase in LDI content. The decrease in the heat of fusion and thermal degradation temperature in both composites was observed.

Cheung et al. (2008) have synthesized the silk fibre reinforced poly(lactic acid) (PLA) composites. It was observed that the biodegradability of silk/PLA biocomposites was altered with the content of the silk fibre in the composites.

Lipsa et al. (2008) have synthesized the biodegradable films of PVA/PLA blends. Poly(lactic acid) was synthesized by melt polycondensation procedure of L(+) -lactic acid using manganese acetate as catalyst. Huda et al. (2008) have synthesized the kenaf fibre reinforced PLA laminated composites by compression molding.

Ghanbarzadeh et al. (2010) have prepared the starch/carboxy methyl cellulose (CMC) composite films by a casting method. The effect of CMC addition on the physical properties of blend films was investigated. The blend film composed of 15% w/w CMC/starch showed the lowest water vapour permeability. The moisture absorption and solubility of the blend films were recorded less. The addition of 20% w/w starch to CMC caused the increase in tensile strength (TS) by 59% in comparison to pure starch film.
Kumar et al. (2010) have studied the woven and nonwoven flax fibre reinforced poly(lactic acid) (PLA) biocomposites. Jonjankiat et al. (2011) investigated the properties of ecofriendly biocomposites prepared from poly(vinyl alcohol) (PVA) and cellulose microfibres (CMF). It was observed that interactions of -OH groups of PVA with CMF molecular chains lead to increase in the melting point and crystallinity of biocomposites. It was observed that the addition of CMF filler increased the shear strength of samples from 1.55 to 2.41 MPa. The increase in the mechanical and thermal properties of sago pith as a bio-filler (SPB) on poly(vinyl alcohol) (PVA) was studied by Yee et al. (2011).

The flexural strength, tensile strength and tensile modulus of the soyprotein-jute fibre composites using water as plasticize were observed higher as compare to polypropylene (PP)-jute fibre composites (Reddy and Yang, 2011). Starch/polyvinyl alcohol (PVA)/titanium oxide (TiO₂) nanocomposite films have been synthesized by casting method (Yun et al., 2012). Sisal fibre (SF) reinforced poly(lactic acid) (PLA) composites prepared by a compression molding technique has been reported by Singh et al. (2011). Two samples of PLA/SF composites were developed with a fibre content of 10 and 20% by weight.

Laxmashwar et al. (2012) have developed the biodegradable composite films of cellulose with poly(vinylalcohol) (PVA). The biocomposite films have shown transparency, flexibility and batter mechanical properties. It also showed the good biodegradability and better barrier properties.

Laxmeshwar et al. (2012) have modified the cellulose by using 2-(Trifluromethyl)benzoylchloride by base-catalyzed reaction. The biodegradable composite films were developed by using modified cellulose with poly(vinyl alcohol). Composite films showed good mechanical and biodegradable properties.

Roy et al. (2013) have evaluated the dielectric properties of PVA/ZnO nanocomposites films. It has been observed that PVA/ZnO nanocomposites behave as lossless materials above $10^6$ kHz. The electrical characterization of sisal powder filled
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poly(vinyl alcohol) (PVA) composites has been investigated. Dielectric measurements of the composite were determined in the temperature ranged from 30 to 150 °C (Nigrawal and Chand, 2012).

2.5. STARCH BASED BIODEGRADABLE COMPOSITE

The use of synthetic polymer materials has caused significant environmental problems. Solid waste from these materials is a major contributor to environmental pollution as it can take thousands of years to degrade. Therefore, a great deal of attention has been given to the development of various biodegradable materials. The worldwide consumption of biodegradable polymers has increased in the last few years. The natural biodegradable materials include packaging materials (trash bags, wrappings, loose-fill foam, food containers, film wrapping, laminated paper), disposable nonwovens (engineered fabrics) and hygiene products (diaper back sheets, cotton swabs), consumer goods (fast-food tableware, containers, egg cartons, razor handles, toys), and agricultural tools (mulch films, planters). Starch based biocomposites can be produced by blending or mixing as different naturals polymers.

Starch-poly(vinyl alcohol) cast films were prepared with and without crosslinking agent (hexamethoxymethylamine) in the absence of plasticizer. Moisture absorbance of the films prepared without crosslinking agent at low relative humidity was similar to that of PVA (Chen et al., 1997). Starch-poly(vinyl alcohol) (PVA) cast films contained 41 % starch, 41 % PVA, 15% glycerol and 3% poly(ethylene-co-acrylic acid) (EAA). The tensile strength (TS), percent elongations at break (%E), tear resistance and impact strength of biocomposite films were made with different types of starches such as normal cornstarch, waxy cornstarch, high amylose cornstarch (50% amylose and 70% amylose), wheat starch, potato starch and tapioca starch have been used for the preparation of films (Lawton, 1996).

Thermoplastic starch (TPS)/cellulose fibre composites have been prepared by using fibres from different sources, such as flax and ramie fibres (Wollerderfor and Bader,
1998), potato pulp fibres (Dufresne and Vignon, 1998; Dufresne et al., 2000), bleached leaf wood fibres (Averous et al., 2001), bleached eucalyptus pulp fibres (Curvelo et al., 2001), wood pulp fibres (Carvalho et al., 2002), and cassava bagasse fibres (Teixeira et al., 2009, Sariffuddin et al., 2012). It was observed that the mechanical properties of TPS/cellulose fibre composites were found to be higher.

Mao et al. (2000) have studied the improvement of properties of cornstarch blended with poly(vinyl alcohol) (PVA) and glycerol. The blending of starch-glycerol with PVA resulted in significant improvement in both tensile strength (TS) and elongation at break. The tensile strength (TS) and elongation at break of starch-glycerol films without PVA was 1.8 MPa and 113%, whereas films containing PVA was 4 MPa and 150%, respectively. Fang and Fowler (2003) have discussed the use of starch and its derivatives as packaging materials. Park et al. (2005) have prepared the starch/polyvinyl alcohol (PVA) blend films by using starch, polyvinyl alcohol (PVA), glycerol (GL) sorbitol (SO) and citric acid (CA).

Imam et al. (2005) have prepared the cohesive and flexible cast films by blending lignocellulosic fibres derived from orange waste and PVA with or without cornstarch. Starch-based trays were produced with a high fibre ratio and PVA showed improved water resistance (Cinelli et al., 2006).

Bamboo fibres were used as reinforcement with biodegradable resin. It was observed that the mechanical properties of biocomposites were found to be higher (Kinoshita et al. (2009). A biodegradable starch/poly(vinyl alcohol) (PVA) blend film for coating the soluble granular fertilizer has been prepared and used as polymeric membranes to control the release rate of fertilizers (Han et al., 2009).

Maiti et al. (2010) have investigated the preparation of green composites of corn starch developed by using resorcinol formaldehyde (RF) as the crosslinking agent. The graft copolymers of Saccharaum spontaneum fibre grafted with methyl methacrylates (MMA) as principal monomer and its binary mixture with acrylamide (AAm), acrylonitrile (AN), acrylic acid (AA) synthesized under microwave were used
as reinforcement. The improvement in the mechanical properties of green composites was observed.

Guimaraes et al. (2010) have studied the tensile strength of composites prepared by starch/banana and starch/bagasse fibre by compression moulding using glycerol and crude glycerine as plasticizers. Majid et al. (2010) have studied the low density polyethylene (LDPE)/thermoplastic sago starch (TPSS)-kenaf fibre composites with the addition of PE-g-MA. The water absorption reduced with the addition PE-g-MA of LDPE/TPSS-kenaf fibre composites. Ramirez et al. (2010) studied the composites based on coconut fibres and cassava and corn starches. The increase in the tensile strength of the composites was observed.

Native starch (corn, potato and waxy corn) and phosphorylated corn starch blended with bagasse fibre and glycerol has been used for the preparation of biodegradable films (Garcia et al., 2011). Azahari et al. (2011) have synthesized the polyvinyl alcohol (PVA) and corn starch blend films by solution casting method. It was observed that the tensile strength and elongation at break decreased with increase in corn starch.

Cellulose fibres from recycled newspaper were used as reinforcement for thermoplastic starch. The composites were prepared from corn starch plasticized by glycerol and cellulose fibre content ranging from 0 to 8% (wt/wt of fibres to matrix). The mechanical, thermal and water resistance properties of composite films were improved (Wattanakornsiri et al., 2011). Biocomposites of thermoplastic sago starch (TPSS) and kenaf core fibre (KF) were prepared at different fibre loading (0-35 wt.%). Thermal and mechanical properties of the composite films were found to be improved (Saffuddin et al., 2012).

Naznin et al. (2012) have investigated the effect of natural polyphenol extract (Acacia catechu) on physicochemical properties of starch/PVA-based film. Acacia catechu extracts were incorporated in the starch/PVA (60:40%) based films at different concentrations (0.1% to 15%). The tensile strength (TS) of the starch/PVA blend film
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was observed 24MPa which increased (33.8MPa) with the addition of acacia. Different percentages of urea (1% to 15%) were incorporated into the starch/PVA/acacia based film. The best tensile strength (11MPa) and elongation at break (59%) were obtained at 5% urea concentration.

2.6. ANTIBACTERIAL PROPERTIES OF NATURAL FIBRE REINFORCED BIODEGRADABLE COMPOSITE

Synthetic and non-biodegradable materials are generally used for food packaging that create serious problem to the environment. There is growing interest in recent times to develop materials with film forming capacity and antimicrobial properties which improve food safety and shelf-life. Antimicrobial packaging is one of the most promising active packaging systems. The use of such packaging not only acts as substitute for good sanitation practices, but also enhances the safety of food as an additional hurdle for the growth of pathogenic or spoilage microorganisms. Antimicrobial packaging is an effective method for the inhibition of certain bacteria in foods. This problem can be controlled by using environmental friendly packaging material based on natural biopolymers. Chitosan, starch and PVA are ecofriendly materials which can be used for active packaging in biomedical application in the form of film.

The antimicrobial activity of films prepared from chitosan/starch/PVA has been tested against three pathogenic microorganisms such as *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Candida albicans*. The films showed fair activity against *Bacillus subtilis*. Antimicrobial films were prepared by blending chitosan and poly(vinyl alcohol) (PVA) with glutaraldehyde as the cross-linker. The microbiological screening of the film has demonstrated the antimicrobial activity against food pathogenic bacteria such as *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus subtilis*. It has been observed that the composite film was a promising material for food packaging applications (Tripathi *et al.*, 2009).
Soy starch and gelatin edible films incorporated with *Myrtus communis* and *Ziziphus spina-chouristi* essential oils were studied for different food applications (orange, apple, lemon, tomato, pizza dough, chicken salami, meat salami, artificial cheese, mayonnaise, yoghurt and skimmed cheese). Antimicrobial activity results against the food pathogenic microorganisms such as *Escherichia coli*, *Salmonella typhimurium* and *Aspergillus niger* by using agar diffusion assay method showed that the films extended the shelf life of the food products (Khalil *et al.*, 2013).

Antimicrobial activity of nanofibre mats obtained from colloidal dispersions of chitosan based blended, with polyvinyl alcohol, loaded with silver and control samples (chitosan/PVA) with different degrees of crosslinking was studied. Samples were compared for their effectiveness in reducing or halting the growth of aerobic bacteria. The results showed superior properties and synergistic antibacterial effects by combining chitosan with silver nanofibre mats (Abdelgawad *et al.*, 2014).

2.7. BIODEGRADABILITY OF NATURAL FIBRE REINFORCED BIODEGRADABLE COMPOSITE

Biocomposites are commonly used for a variety of applications such as mulch films, greenhouse construction materials, packaging materials, etc. The plastic materials are not easily degradable and remain in the environment for long time. As a result, interest in the use of natural biodegradable polymeric materials has grown considerably.

Biodegradation of polymeric materials based on polyvinyl alcohol and starch was studied in soil. Polyvinyl alcohol and starch base polymeric materials showed increased biodegradation properties (Tudorachi *et al.*, 2000). Starch/polyvinyl alcohol/ glycerol films were prepared by casting method. For biodegradation studies starch/glycerol samples were incubated in compost soil. It was observed that samples lost up to 70% of their dry weight within 22 days. The addition of polyvinyl alcohol lowered the rate and extent of biodegradation (Mao *et al.*, 2000). Imam *et al.* (2005a)
have studied the biodegradability of starch/PVA blend films reinforced with orange waste. The addition of a crosslinker lowered the overall extent of degradation in composites. It was observed that CO$_2$ production was significantly higher in blends with PVA. It suggests that the presence of starch and orange fibre stimulates PVA degradation in soil.

Imam et al. (2005b) have prepared the cast films of cellulosic fibres derived from orange waste and PVA. It was observed that the films were biodegraded in 30 days in soil. Corn starch was introduced as a biodegradation promoter and gluing component (22% by weight) to the hybrid composite.

Respirometric test revealed that soil microbes preferentially used natural polymers and low molecular weight additive as a carbon source compared to biodegradable polymer (Cinelli et al., 2008). Biodegradability of woven and nonwoven flax fibre reinforced poly(lactic acid) (PLA) biocomposites was observed. It showed the biodegradation with 20-25% loss in weight after 50-60 days. In the presence of dicumyl peroxide as additive, biodegradation of the composites was relatively slow (Kumar et al., 2010). Azahari et al. (2011) have prepared corn starch and polyvinyl alcohol blends films using the solution casting method. The biodegradability of the films was investigated based on enzymatic absorbency in water, acidic solution and soil burial method. The films containing corn starch were found to be more highly biodegradable by enzymes as well as in soil and compost as compared to a film without corn starch.

The biodegradability of films prepared with Acacia catechu extracts (0.1% to 15%) and urea (1% to 15%) incorporated in the starch/PVA (60:40%) based film were studied by Naznin et al. (2012). The soil burial test of 70 days showed that the urea incorporated film showed 91% degradation as compared to non urea incorporated films (94%).