Wood is an important naturally occurring renewable resource material finding widespread use in industry. Its major uses are in the preparation of traditional structural materials, which are utilized for the construction of houses and furniture. In less advanced societies most of the wood is used as a fuel. For preparing low cost houses and furniture, wood is preferred over iron, cement and the like because of its certain valuable properties such as low thermal conductivity, high electrical resistivity, superior resistance to corrosion, high sound absorption, high strength to weight ratio, ease of procurement and workability to the desired shape and size, etc. Man, therefore, learnt to use wood and appreciated many of its virtues such as the warm friendly feel, the beauty of the natural color and grain of different species. However, because of the tremendous increase in the needs of the present day human civilization in diversified areas, the supply of the sawn timber could not keep in the balance with the amount of the required material. An alternative had to be looked upon which could fill the gap between the required product and the material to be used. This led to the development of wood based polymer composites.

The most common type of particle board is produced from wood chips obtained from timber, mill waste and the like. Steep demand is a feature of the present wood based panel board industry; still it is trapped under the threshold of natural death because of the gradual erosion of raw material. In view of the declining forest resources, it is essential that every possible step should be taken to find out suitable substitutes of timber to meet the rapidly increasing needs for particle boards in future. In this regard utilization of the vast amount of agricultural wastes in the production of board materials would not only solve the disposal problems of the same in an agricultural
country like India, but also would ensure rich dividends to the rural poor and thus help to develop the rural economy by setting up small scale particle board industries based on agro wastes.

Particle boards made from jute sticks and similar raw materials are in commercial use as ceiling tile and the like. They don't have that strength properties and water resistance of wood based particle boards. In view of preserving the forest resources and for maintaining ecological balance, agro waste based particle boards have shown promise as substitute of timber based. In that connection pine needle cellulose can definitely play a substantial role.

In the present work, lignocellulosic fibrous material from pine needles a forest waste product of conifers has been utilized for the preparation of particle boards using synthetic resins such as PF, UF and PRF. In addition to this, the lignin extracted from the mother liquor of the digested pine needles has been utilized as additive to phenol-formaldehyde resin. The use lignin based PLF resin is supposed to decrease the use of expensive component, phenol. The whole work is distributed to in four chapters.

**Chapter 1**: - The chapter discusses on the comprehensive review on preparation of particle board from different raw materials using different methods.

**Chapter 2**: - This chapter refers to the basic materials required for the preparation of the particle boards. The chapter is therefore divided into two sections i.e. Section A and Section B.

**Section A** deals with the raw cellulosic material, referred to as the reinforcing agent. A brief discussion on the different cellulosic materials used for the particle board is undertaken. The use of pine needles as the reinforcing agent in this section has been
discussed. Characterization of the pine needles w.r.t. physical and chemical analysis has been given.

The experimentation involves the collection, chopping and the digestion of pine needles. After collection, the needles were air dried and chopped to a size of 0.5” to 1.0”.

The dried chopped and weighed pine needles (5 kg) were put in the digester. To it was added 50 liter of 5% aqueous solution of NaHSO₃. The digester was closed air tightly and the needles were allowed to digest for 8 hour under pressure. After the specific time, the pressure was released and the needles were removed from the digester.

The digested needles were thoroughly washed with water and allowed to dry in the open. In between, while the needles were still wet, a mild thrashing was given with a wooden hammer to separate the cellulosic fibers. They were allowed to dry in air and then in the oven at 60-70°C. The moisture content of these pine cellulosic fibers is maintained between 6-8%. These fibers were used as a reinforcing agent in the preparation of particle boards.

The pine cellulosic fibers obtained after the digestion of the pine needles have been characterized by, IR Spectroscopy, thermogravimetric analysis and water absorption studies from the atmosphere and after the samples were immersed in water. The IR spectra showed a band between 3300-3600 cm⁻¹ due to H-bonded hydroxyl groups of the cellulose. The TGA analysis shows that the Pn-cellulosic fiber undergoes thermo-oxidation process with formation of flammable volatile glycosan.

Section B deals with second and the most important component of polymer composites i.e. the matrix constituting the resins, which holds and binds the
reinforcing agent. Following matrices have been used for the preparation of particle boards from pine-cellulosic fibers:

**Phenol – Formaldehyde**

**Urea – Formaldehyde**

**Phenol – Resorcinol – Formaldehyde**

**Phenol – Lignin – Formaldehyde**

A comprehensive literature on the utilization of these resins in the manufacture of the particle boards has been reviewed. Various additives and the role they play in improving the characteristics of a polymer resin to function efficiently as an adhesive has also been discussed. Chemistry, method of preparation and properties of these adhesives have been discussed. The resins were characterized with respect to the pH, flow time, curing time and solid contents of each resin. The phenol-formaldehyde resin was found to be the best among all the resin w.r.t. different properties studied.

**Chapter 3:** The present chapter, deals with the modification of the pine ligno-cellulosic fibers through graft copolymerisation using chemical and radiation methods.

Copolymerization is the most general and powerful method of effecting modifications in polymers and is widely used in the production of commercial polymers. Among various methods, graft polymerization method is simple and easy to handle. The pine needles were treated as discussed in chapter II to separate the cellulosic fibers and were further used for grafting reactions.

(i) Graft Copolymerization of methyl acrylate (MA) and ethyl acrylate (EA) onto Pn-cellulosic fiber was carried out by the chemical method, using potassium
persulphate (KPS) and Ferrous ammonium sulphate (FAS) as redox initiator. Crushed, dried Pn-cellulosic fibers (0.100 gm) were suspended in 50 ml of deareated water in a three-necked flask placed in a water bath maintained at a definite temperature. A known amount of potassium persulfate and ferrous ammonium sulfate was added to the flask. The reaction flask was flushed with nitrogen gas for 30 min. prior to the addition of the monomer. A definite amount of monomer (MA/EA) was added to the reaction flask and graft copolymerization was carried out for a definite time period at varying temperatures under nitrogen atmosphere. After the stipulated time period, the reaction mixture was filtered and extracted several times with acetone for the removal of the homopolymer [Poly (MA)/Poly (EA)]. The homopolymer free grafted fibers were dried in a vacuum oven at 50°C. Percentage of grafting was determined from the increase in weight of the fiber as follows:

\[
\% \text{ Grafting (} P_g \text{)} = \frac{W_1 - W_0}{W_0} \times 100
\]

Where \( W_0 \) and \( W_1 \) are respectively the weights of the original fiber and grafted fiber after complete removal of the homopolymer. Percentage of grafting has been studied as a function of various reaction parameters such as (i) concentration of KPS and FAS, (ii) concentration of monomer, (iii) temperature, (iv) time of reaction, and (v) amount of Pn-Cellulosic fibers. Maximum \( P_g \) of 73% and 82% for MA and EA respectively was obtained at [MA]=22.2 \( \times 10^{-2} \) mol/L and [EA]=18.42 \( \times 10^{-2} \) mol/L, at 60°C within 3h. Graft copolymerization of MA and EA has also been carried out.
in presence of binary mixture of water and alcohol as reaction medium. The effect of
different alcohols such as methanol, ethanol, butanol and isopropanol on percentage
of grafting of MA and EA has been studied as a function of alcohol concentration in
the binary solvent system. All the alcohols were found to decrease the percentage of
grafting of both MA and EA than that obtained in aqueous medium under optimum
conditions.

(ii) Graft Copolymerization of Styrene onto Pn-cellulosic fiber by Gamma
Radiation Induced method using gamma radiations from Co-60 source housed in
Gamma Chamber-900.

Crushed, dried Pn-cellulosic fibers (100 mg.) were suspended in 25 ml. of deaerated
distilled water in a beaker. A definite amount of the monomer (styrene) was added to
reaction mixture and placed in the gamma chamber, the reaction was allowed to
continue for a definite time period a constant dose rate of 0.43 kGy/h. After the
stipulated time period, the reaction mixture was filtered and extracted several times
with benzene to remove the homopolymer i.e. poly (styrene). The homopolymer free
grafted fibers were dried in vacuum oven at 50°C. Percentage of grafting was
calculated as discussed above.

Percentage of grafting has been studied as function of various reaction parameters
such as concentration of monomer; reaction time, amount of water and amount of
Pn-cellulosic fibers. Maximum grafting (33%) was obtained at [Sty] = 57.74 X10^-2
mol/L when 0.100g of fibers used. Graft copolymerization of styrene has also been
carried out in the presence of binary mixture of water and alcohol as the reaction
medium. Effect of different alcohols on percentage grafting of styrene has been
studied as a function of amount of alcohol in the binary solvent system. Percentage of grafting increases in the binary solvent system except for isopropanol than that obtained in aqueous medium.

**Evidence of Grafting:** The formation of the graft copolymer has been identified by IR spectral analysis, thermogravimetric analysis and water absorption behavior and comparing the same with the ungrafted samples. The grafted fibers i.e. PnCell-g-poly (MA) and PnCell-g-poly (EA) showed an additional band in the region 1710 cm⁻¹ due to >C=O of grafted polymeric chains of poly MA/polyEA and PnCell-g-poly (Sty) showed bands in the region 1451 cm⁻¹ and 755 cm⁻¹ due to >C=C stretching of aromatic ring in addition to the associated bands between 3300-3600cm⁻¹ due to H-bonded hydroxyl group of cellulosic in the Pn-Cellulosic fibers.

The IDT, FDT and DT at every 10% weight loss of MA and EA grafted Pn-Cellulosic fibers are less than that observed for unmodified fibers indicating that grafting decreases the thermal stability. However, the reverse observation is made for styrene grafted Pn-Cellulosic fibers which, therefore indicates grafting of styrene increase thermal stability.

All the grafted polymers i.e. poly (MA), poly (EA) and poly (Sty) are hydrophobic in nature and are expected to impart this property to the cellulosic fibers. Water absorption studies reveal that grafting of MA, EA and Styrene has reduced the percent water absorption as compared to that observed for unmodified Pn-Cellulosic fibers. The utilization of the grafted Pn-cellulosic fiber in the preparation of particle boards therefore, is expected to have improved hydrophobic properties.
Chapter 4 :- This chapter describes the preparation of polymer based composites i.e. particle boards from Pine-Cellulosic fibers and the resins such as phenol-formaldehyde, urea-formaldehyde, phenol-resorcinol-formaldehyde and phenol-lignin-formaldehyde. The characterization of the particle boards with respect to mechanical properties such as tensile strength perpendicular and parallel to surface, modulus of elasticity, modulus of rupture and water absorption behaviour has been made.

Method of preparation of particle board: Definite amount (1000g) of pine cellullosic fiber of known moisture content (6%) were intimately mixed with the specific amount of the resin in a glue mixer and allowed to stand in air for half an hour so that the moisture content of the mix is between 10%-25%. This depends upon the nature of the resin used i.e. PF, UF, PRF, or PLF, mole ratios of the resin components and the amount of the resin used. After thorough mixing of the cellullosic fibers and the resin, the mixture was placed in a wooden frame placed on aluminium sheet for mat formation. The wooden frame was replaced by another iron frame of 10 mm thickness and was covered with another aluminium sheet from above. The surfaces of the aluminium sheets were coated with oleic acid from inside to avoid adhesion of the mix to the sheets and an easy removal of the particle board after its production. The whole assembly was then placed inside the hot press for specific time, temperature and pressure depending upon the nature of the resin used. After removing from the press, the aluminium sheets and the iron frame were removed. The particle board were kept in the open for conditioning at room temperature. The sides of the boards were trimmed by D.D. saw to give smooth edges.
Characterization of particle boards: Each particle board, prepared by using different resins, was characterized with respect to water absorption and mechanical properties such as tensile strength both perpendicular and parallel to surface, modulus of elasticity and modulus of rupture according to the procedure adopted by Bureau of Indian Standards.

From the data analysis of each of the particle board, it is concluded that the water absorption and mechanical properties are best for the boards prepared by using 450g PF resin with F/P mole ratio of 2.44. Percent water absorption 11.25 % and 25.82 % after 2h and 24h is minimum as compared to all other boards. Minimum values of percent thickness expansion and percent length expansion have been observed for the minimum value of water absorption suggesting that dimensional stability is directly linked with the water absorption property. Boards prepared with the PF resin also showed better mechanical properties than boards prepared from other resins. Maximum T.S. perpendicular to the surface (0.059 N/mm^2) and T.S. parallel to the surface (0.095N/mm^2) and maximum MOR (5.1N/mm^2) and MOE (693.8N/mm^2) is obtained for PF treated boards. UF resin of 1.74 mole ratio and 425gm of it shows good results among different ratios of UF but is dimensionally and mechanically less stable than PF resin. On comparing the properties of particle boards from modified PF resin (i.e. PRF & PLF) with particle boards from PF resin, it was observed that the boards are mechanically and dimensionally less stable than particle boards from PF resins.

On the basis of the results and comparison of the properties of the particle boards, the following order for resins to give particle boards of best quality is observed
PF > UF > PLF > PRF

PRF resin bonded boards should have better water resistance and strength properties than those of UF and PLF bonded material. Lower amount of PRF resin used as binder to produce the boards may be responsible for the lower values of the above properties.

In order to ensure the effect of thickness on the mechanical properties of particle boards, particle boards of 5mm thickness were prepared from 500gm of pine cellulosic fibers using 225gm of PF resin of 2.44 F/P mole ratio. The amount of the fibers and the resin were half the amount used for preparing 10mm thick particle boards. Similar boards of 5mm thickness were also prepared from grafted pine cellulosic fibers. Water absorption of 5mm thick particle boards both after 2h and 24h water treatment is higher (22.35% and 32.07%) than that observed for 10mm thick particle boards (19.20% and 31.12%). This may be due to the reason that penetration of water to the bulk of 10mm thick particle board will be lesser and therefore these boards show lower water absorption values. The particle boards of 5mm thickness from pine needles grafted with methylacrylate and ethylacrylate however show lower percent water absorption both after 2h (18.12% and 17.35%) and 24h treatment (28.26% and 28.61%) respectively than 5mm and 10mm thick particle boards, from the ungrafted pine cellulosic fibers. The thickness parameter has not affected the water absorption behaviour in these modified fibers boards. Tensile strength parallel and perpendicular to the surface of 5mm particle boards is much lower (0.037 N/mm² and 0.021 N/mm²) as compared to 10mm thickness particle boards (0.10 N/mm² and 0.059 N/mm²) suggesting that an optimum thickness of the board is an
important factor for T.S. properties. The MOE (590.54 N/mm\(^2\)) of particle boards of 5mm thickness is also lower than 10mm thick particle board (693.82 N/mm\(^2\)). However, the MOR of 5mm particle boards is little higher (5.65 N/mm\(^2\)) than that of 10mm (5.10 N/mm\(^2\)).

All these properties suggest that the thickness of the particle board is an important factor for achieving the product of high quality with standard properties. A change in the ingredients ratios i.e. amount of reinforcing agent to resin, the quality of the resin, addition of additives, thickness etc. is likely to give particle boards which can match the standards laid by Bureau of Indian Standards.

Detailed studies of the present work on the application of pine needle cellulose as the raw material for the production of particle board show that though the products made by using resin adhesives like PF, UF, PRF & PLF with pine needle cellulose do not conform to IS specification, they have considerable potential for further improvement to reach the goal. By using wax emulsion along with the resin adhesive as well as by the lamination of the board material, moisture resistance and strength properties of the products can be considerably increased.