Chapter 3
Experimental
3.1.0.0 Materials Used

a) Ammonium dihydrogen orthophosphate supplied by Himedia Laboratories Pvt. Ltd., Mumbai, India.

b) Ammonium polyphosphate supplied by Himedia Laboratories Pvt. Ltd., Mumbai, India.

c) Cetyltrimethylammonium bromide supplied by Himedia Laboratories Pvt. Ltd., Mumbai, India.

d) 4-Dimethylaminopyridine supplied by Himedia Laboratories Pvt. Ltd., Mumbai, India.

e) Dimethyl urea supplied by Himedia Laboratories Pvt. Ltd., Mumbai, India.

f) Dimethylol urea supplied by Sigma Aldrich.

g) Guanidine nitrate supplied by Himedia Laboratories Pvt. Ltd., Mumbai, India.

h) Melamine supplied by Acros Organics.

i) Microcrystalline cellulose supplied by Acros Organics, USA.

j) N,N-Dimethylformamide supplied by RFCL Limited, Delhi.

k) Pentaerythretol supplied by Himedia Laboratories Pvt. Ltd., Mumbai, India.

l) Pyridine supplied by Qualigens Fine Chemicals, Bombay.

m) Thiourea (Himedia Laboratories Pvt. Ltd., Mumbai, India)

n) Triethylamine supplied by Acros Organics, New Jersey, USA.

o) Urea (Himedia Laboratories Pvt. Ltd., Mumbai, India).

3.2.0.0 Material Preparation for Thermal, Flammability and Kinetic Studies of Wood Veneers

Wood veneers of Eucalyptus, Poplar and Mango are used in manufacturing of plywood in India and Gurjan is used as a face to decorate plywood. These wood veneers were collected form Galaxy Plywood Industry, Yamunanagar, Haryana, India. Wood veneers were washed with water to remove water soluble impurities and were dried in an oven at 70 °C under vacuum. The samples were powdered by sawing. The powdered samples were placed in desiccators to prevent them from absorbing moisture. TG analysis of these samples was performed at multiple heating rates in nitrogen atmosphere from ambient to 700 °C temperature. Veneers of the sizes (L×W×T) 100×6×2.5 mm³ and 125×13×2.5 mm³ were cut for the purpose of LOI and UL 94 testing, respectively.
3.3.0.0 Impregnation of Guanidine Nitrate over Poplar Wood with Catalytic Amount of Bases

Poplar wood veneer samples sizes (L×W×T) 150×100×2.5 mm³, were immersed into hot water for 1 h in order to vacate pores from water soluble substances and dried under vacuum. Minimum three wood specimens were used for each impregnation condition. Samples were prepared by dipping water treated wood samples into 20% w/v hot aqueous solution of guanidine nitrate (GUN) for 30 min. Other samples were obtained by dipping wood into 20% w/v hot aqueous solution of guanidine nitrate in presence of bases such as N,N-dimethylformamide (DMF), 4-dimethylaminopyridine (DMAP), pyridine (Py) and triethylamine (TEA) for 30 min and were dried under vacuum until they do acquire constant mass. Untreated Poplar wood sample was named ‘virgin wood’ and sample impregnated with guanidine nitrate only was designated as ‘wood-GUN’. Samples impregnated with guanidine nitrate in presence of DMF, DMAP, Py and TEA were designated as wood-GUN-DMF, wood-GUN-DMAP, wood-GUN-Py and wood-GUN-TEA, respectively.

3.4.0.0 Impregnation of Cetyltrimethylammonium Bromide (CTMAB) and Ammonium Dihydrogen Orthophosphate (ADHOP) Blends on Poplar Wood

The Poplar wood veneer sample sizes (L×W×T) 150×100×2.5 mm³, were immersed into hot water for 1 h in order to make wood free from all types of water soluble impurities and dried under vacuum until they do acquire constant mass. Three samples were used for each impregnation condition. Impregnation of chemicals on wood veneer surface was done by dipping in hot solution of varying composition of CTMAB and ADHOP at 8% w/v concentration for 30 min and samples were dried in oven under vacuum. The samples were named as virgin wood, wood+8%CTMAB, wood+2%ADHOP+6%CTMAB, wood+4%ADHOP+4%CTMAB, wood+6%ADHOP+2%CTMAB and wood+8%ADHOP, respectively.

3.5.0.0 Impregnation of Tetrakis(hydroxymethyl)phosphonium Chloride (THPC) and THPC/Urea/Urea Derivatives Blends on Poplar Wood

Tetrakis(hydroxymethyl)phosphonium chloride (THPC) was prepared by reacting phosphine with an aqueous solution of formaldehyde and hydrochloric acid in our lab and reported in papers [129-131]. Samples were prepared by dipping oven dried water treated samples sizes (L×W×T) 150×100×2.5 mm³ into a hot solution of
40% v/v THPC and 20% w/v urea for 30 min. The treating solution was neutralized by NaOH solution and pH was maintained 6-7. Then samples were cured at 160 °C for 5 min in oven. Other samples were prepared in the same manner by taking thiourea, dimethyl urea (DMU) and dimethylol urea (DMOU) at place of urea. Samples of this series were designated as virgin wood, wood-THPC-urea, wood-THPC-thiourea, wood-THPC-DMU and wood-THPC-DMOU according to the blending solution.

3.6.0.0 Coating of Fly Ash-Intumescent Composites over Poplar Wood

Intumescent (int) formulation was comprised of 18% Ammonium polyphosphate (APP), 6% Melamine (MEL) and 6% w/w Pentaerythretol (PER) of wood, respectively. Other formulations were prepared by addition of FA at different loading level i.e. 2%, 4%, 6% and 8% w/w of intumescent formulation. Acrylic resin was used as binder and was 50% w/w of formulation. The solid mass content of resin was 50%. The paste of formulations was prepared by simple mixing using water as wetting agent in pastel mortar. The viscosity of all formulations was adjusted accordingly by wetting agent. The mixture was painted by brushing over surface of wood sample sizes (L×W×T) 150×100×2.5 mm³ and cured at 120 °C temperature in oven for five min. The samples were named as virgin wood, wood-int, wood-int-2% FA, wood-int-4%FA, wood-int-6%FA and wood-int-8%FA corresponding to loading level of fly ash into intumescent formulation.

3.7.0.0 Studies/Techniques Used

3.7.1.0 Scanning Electron Microscopy (SEM)

The SEM micrographs of silver coated selected samples were analyzed by SEM model EVO 50 with an accelerating voltage of 20 kV.

3.7.2.0 Elemental Analysis

The elemental analysis (CHN) was performed on a Thermo Finnigan Flash EA TM1112 analyzer to investigate mass percentage of carbon (C), hydrogen (H) and nitrogen (N) elements of wood and modified wood samples.
3.7.3.0 Thermal Analysis

TG, DTG and DTA of wood and modified woods were carried out at multiple heating rates under dynamic nitrogen/air from ambient to 700 °C temperature by Perkin Elmer Diamond TG/DTA analyzer. TG analysis of each sample was performed three times under same conditions. The resolution of this instrument is 0.02 μg as a function of temperature. Samples milled passing 75 meshes were used for thermal analysis. The TG/DTA analyzer was calibrated before recording thermograms. Dried alumina powder was used as a reference material and ceramic sample holder was employed for taking thermograms. In order to ensure the uniformity of temperature of the sample and good reproducibility, small amounts (3-6 mg) were taken.

TG curves were analyzed by using Pyris software from TG analyzer and data was used in MS Excel and origin software to calculate degradation activation energy (E) and correlation coefficient (R²) by ‘model free’ methods Kissinger [114], Friedman [115], Ozawa-Flynn-Wall (O-F-W) [116,117] and Coats-Redfern (modified) [118,119].

3.7.4.0 Limiting Oxygen Index (LOI)

LOI is the minimum amount of oxygen in oxygen-nitrogen mixture required to support complete combustion of a vertically held sample that burns downward from the top. The higher the LOI value, more effective is the flame retardant. The LOI values of wood and modified woods were determined in accordance with ASTM D 2863 standard with Platon S. A. Associates Oxygen Index apparatus. Samples sizes were (L×W×T) 100×6×2.5 mm³ for this test.

3.7.5.0 UL 94 (horizontal burning test)

The flame spread rate of all the samples was investigated by the horizontal burning (HB) test according to the UL 94 test standards. A set of three samples sizes 125×13×2.5 mm³ were used to investigate horizontal flame spread rate between two bench marks at 25 mm and 100 mm position. The specimen was mounted on a stand oriented in the horizontal direction with its thickness vertically and flame is applied to the free end of the specimen. The flame spread or burning rate (mm min⁻¹) was calculated using the following formula:

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\text{Flame spread rate} = \frac{100}{t - t_1}
\]
where $t_1$ is the burning time from the beginning to 25 mm, and $t$ is the burning time from the beginning to 100 mm benchmark. The status and other details of this have been discussed earlier in the introduction part of thesis (1.10.3.0).