# Dimensional Stability and Thermal Property Improvement of Pinusradiata D. Don by Double Step Chemical Modification using Fyrol 51 and Propylene Oxide

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Abstract—The hygroscopic nature of wood can be explained by the presence of hydroxyl groups present in cellulose and hemicellulose and their ability to form hydrogen bonds. The substitution of (-OH) in wood can be achieved in several ways, including chemical modification. In the present study Pinusradiata wood samples were modified by single step using propylene oxide (PO) with Triethyl amine as catalyst (95/5) ratio w/w) and by double step modification first with Fyrol51(Dimethyl Methylphosphonate), fire retardant, by pressure treatment followed by chemical modification using propylene oxide (PF). The two step modification will ensure saturation of fire retardant in cell wall and fixation with chemical modification. Physical parameters like Weight Percentage Gain (WPG), Water absorption, Volumetric Swelling (S), Anti Swelling Efficiency (ASE) and thermal property viz thermal conductivity and resistivity was studied. WPG for samples of Pinusradiata subjected to PF and PO treatment was 31.45% and 30.16% respectively. Water absorption for PF and PO modification was significantly different from each other till 336hrs with 75.49% and 82.51%, which was lower than untreated samples with 143.26% absorption. Volumetric Swelling for PF modification was significantly lower from PO and control samples. ASE for PF treated samples was in range of 75.80-67.92% which was significantly more than PO treated samples with ASE of 69.84-62.64%. Lowest oven dried thermal conductivity was observed using for PF (0.058W/mK) followed by PO (0.064W/mK) and control (0.076W/mK). Whereas highest thermal resistivity was for PF (17.241mK/W) followed by for PO (15.873mK/W) and control samples had lowest value (13.158mK/W). The two step chemical modification using Fyrol51 as fire retardant and Propylene oxide resulted in better dimensional stability and thermal property than PO modification. Thus the double step chemically modified wood may be applied in building as insulator inform of external used as insulator in buildings.

**Keywords**: Chemical modification, Fire retardant, Propylene oxide, Fyrol 51, Dimensional stability, Thermal Conductivity.

## 1. INTRODUCTION

Wood is a complex composite biological material, with some extraordinary chemical and mechanical properties. These properties of wood and its fibres are due to its chemistry and anatomical structure. In spite of several advantages of wood, they have certain properties which are undesirable as building material. The hygroscopic nature of wood can be explained by the presence of (-OH) groups present in cellulose and hemicellulose and their ability to form hydrogen bonds [23]. The water molecules get adhered to these hydroxyls groups causing swelling and removal of water molecules causes shrinkage. Moisture swells the cell wall and the wood expands until the cell wall is saturated with water. The swelling and shrinkage of wood due to adsorption and removal of water leads to dimensional instability in wood.

Wood being anisotropic the shrinkage and swelling varies in different direction of wood from same tree and it shrinks or swells most in the direction of the annual growth rings (tangential direction), about half as much across the rings (radial direction), and only slightly along the grain (longitudinal direction) [4]. Average values for shrinkage is approximately 0.4% (0.1-0.5%) for longitudinal direction, 4.0% (1.1- 6%) for radial direction and 8.0% (3.3-14.8%) for tangential direction. The Volumetric shrinkage is almost 12%, but varies greatly among wood species [10].

The substitution of hydroxyl groups in wood can be achieved in several ways, including chemical modification by means of small organic molecules, formation of wood- polymer composites by impregnation of solid wood with water soluble, thermosetting resin systems or organic vinyl monomers in the presence of some cross-linking agents trailed by in-situ polymerization [1].

Various types of chemical compounds have been used for modification of wood including anhydrides, acid chlorides, carboxylic acids, isocyanates, aldehydes, alkyl chlorides, lactones, nitriles and epoxides [17, 2].

Chemical wood modification of wood improves properties like dimensional stability, biological durability, surface hardness and wear, hygroscopic nature, thermal properties and colour [7] stability towards UV- radiation and improvement of weathering performance [2].

# Propylene oxide: Epoxide modification

The reaction between epoxides and the hydroxyl groups is an acid- or base-catalyzed reaction, but most of the work done has been alkali catalysed. The organic tertiary amines are used as catalyst in most cases. The reaction between the wood hydroxyl group and alkylene oxide is fast, produces no residual byproducts, forms stable ether bonds, and can be catalysed by a volatile organic amine. After the initial reaction with a cell wall hydroxyl group, a new hydroxyl group originates from the epoxide system. From this new hydroxyl, a polymer begins to form. The presence of alkoxyl ions in the wood, the chain length of the new polymer shortens owing to chain transfer [16, 15].

$$\begin{array}{c} O \\ R-CH - CH_2 + HOR' - OH - \\ Cat. \\ Epoxide \\ Wood \\ \end{array} \begin{array}{c} OH \\ Cat. \\ OH \end{array}$$

Figure1: The reaction of epoxide with wood (R= CH<sub>3</sub> for Propylene oxide; R'= Wood) [20]

# Dimethyl methylphosphonate (DMMP) or Fyrol 51

Dimethyl methylphosphonate (DMMP) is a colorless organophosphorous flame retardant. DMMP is also used as anti-foaming agent, plasticizer, stabilizer, textile conditioner, and an additive for solvents as well as a catalyst and a reagent in organic synthesis. Phosphorus based flame retardants change the thermal degradation processes in wood as they reduce the temperature at which pyrolysis occurs by increasing the amount of residual char. Increase in dehydration and char formation reduces combustion rate. During combustion phosphorus compounds are acid precursors and forms acids that selectively decompose wood[4].

Thermal conductivity denoted by 'k' is a measure of the rate of heat flow (W m<sup>-2</sup> or Btu h<sup>-1</sup>ft <sup>-2</sup>) through a material subjected to unit temperature difference (K or °F) across unit thickness (m or in.) under steady state condition. Thermal conductivity of wood is much more less than the conductivity of metals with which wood is generally compared in construction. Thermal resistivity is reciprocal of the thermal conductivity and is represented by "R value," Thermal resistance is thermal resistivity times the thickness of the wood. The thermal conductivity of wood depends on several factors: density, moisture content, extractive content, grain direction, structural irregularities such as checks and knots, fibril angle, and temperature. Thermal conductivity increases as density, moisture content, temperature, or extractive content of the wood increases [5].

Thermal conductivity is nearly the same in the radial and tangential directions. But MacLean *et. al.*, 1941 [12], observed

that thermal conductivity higher in longitudinal direction than in the radial or tangential direction. Though, conductivity along the grain is greater than conductivity across the grain by a factor of 1.5 to 2.8, with an average of about 1.8 [5].

In the present paper Propylene oxide was used for chemical modification to study the improvement in dimensional stability and thermal property.

# Materials and methodology

Samples of different sizes as given in Table 1 were prepared from sapwood of seasoned *Pinusradiata* planks. The samples free from knots, mould, stain and any other defects were selected for the study different.

Table 1:	Sample	size for	different	experiments

Sl. No.	Parameter under study	Sample size (mm)	
1.	Weight Percentage Gain (WPG)		
	Radial	50x20x20 (RLT)	
	Tangential	50x20x20 (TLR)	
	Volumetric	60x20x20 (LTR)	
2.	Water Absorption		
	Radial	50x20x20 (RLT)	
	Tangential	50x20x20 (TLR)	
	Volumetric	60x20x20 (LTR)	
3.	Dimensional Stability- Volumetric Swelling-Water Soak method		
	Radial	50x20x20 (RLT)	
	Tangential	50x20x20 (TLR)	
	Volumetric	60x20x20 (LTR)	
4.	Thermal Conductivity	300x300x25	

## **Chemical modification:**

*Pinusradaita* samples were oven dried in hot air electric oven at  $103 \pm 2^{\circ}$ C till constant weight were achieved, and oven dried weight and dimensions were measured.

Chemicals used for the experiments:

1. Propylene oxide 2. Dimethyl methyl phosphonate (DMMP) or Fyrol 51

The treatment was divided into two methods: Single step chemical modification and Double step chemical modification.

- 1. Single step chemical modification: A chemical mixture Propylene oxide and Triethyl amine (95/5 ratio w/w), as catalyst, was prepared for the treatment [7]. Oven dried samples were chemically modified with respective mixture at temperature 120 °C and pressure 10.55 kg/cm<sup>2</sup> (150 lbs/inch<sup>2</sup>) [17]. Samples were treated with Propylene oxide are represented as PO.
- **2. Double step chemical modification**: Double step chemical modification includes following two steps:
- a. Pressure impregnation of samples with DMMP or Fyrol 51 (10% conc): The treatment of DMMP was done by Full

cell pressure impregnation. This method is essential to achieve maximum absorption by the cells and saturating the cell walls with the chemical. The samples were treated in a pressure treatment cylinder by applying initial vacuum of 40cm Hg for 30 mins. At the end of vacuum period, the preservative was introduced into the cylinder, at the end of vacuum. When the cylinder was completely filled with the chemical a pressure of 7 kg/cm<sup>2</sup> (100 lbs/inch<sup>2)</sup>. The pressure was held for 60 minutes, after which the preservative was drained from the cylinder and a final vacuum of 25 cm of mercury for about 15 min. to remove excess chemical.

b. Chemical modification of samples with PO: The samples, pressure treated with Fyrol 51 as mentioned above were chemically modified with chemical mixture of Propylene oxide and Triethyl amine (95/5 ratio w/w), as catalyst, at temperature 120 °C and pressure 10.55 kg/cm<sup>2</sup> (150 lbs/inch<sup>2</sup>) [17]. Samples treated with Propylene oxide and Fyrol51 are represented as PF.

Excess chemical was drained and collected; weight and dimensions of saturated samples were taken. The samples were then oven dried to and weight and dimensions were recorded to ascertain changes in physical properties.

#### Weight Percent Gain (WPG)

Radial, tangential and volumetric samples were prepared as described above to study the weight percent gain due to chemical modification. The treated along with untreated or control samples were oven dried at  $103 \pm 2^{\circ}$ C till constant weight was achieved.

The weight percent gain (WPG) each of specimen was calculated by:

$$WPG = \left[\frac{(Wt - Wo)}{Wo}\right] X100$$

Where Wo and Wt are the oven dried weight of unmodified and chemically modified wood sample respectively.

## Water absorption

To study samples were prepared as described above and were chemically. After treatment the samples were oven dried and weighed (Wd). The samples were submerged in distilled water for 1 to 336 hrs (14 days) constituting 17 cycles. Samples were removed from water at regular intervals and excess adhered water was wiped off with and samples were weighed (Wt) to calculate values water absorption and again submerged for next time interval[1]. Water absorption percentage was determined by:

*Water absorptrion* (%) = 
$$\frac{Wt - Wd}{Wd} X$$
 100

Where Wt and Wd are weight of wood sample soaked in water and oven dried weight of sample respectively.

# Dimensional stability: Volumetric swelling coefficient and Anti Swelling Efficiency

Dimensional stability was determined by estimating volumetric swelling coefficient (S) and Anti Swelling Efficiency (ASE) by simple water soaking method at room temperature. Samples are vacuum impregnated with distilled water for 30 mins then released for 1 hour; vacuum is reapplied for 30 mins and then released for 24 hours [19,13]. Excess water was drained, weights and volumes were measured. Specimens were again oven dried for 48 hours, and their weights and volumes were determined. Volumetric Swelling Coefficient (S) was calculated as the percentage of volume increase compared to oven dried samples due to water soaking using the following formula.

$$S(\%) = \frac{Vs - Vo}{Vo}X \ 100$$

Where V is the volume of saturated sample and Vo volume of oven dried sample.

The ASE of the treatment was calculated from the wet and oven dried volumes of treated and untreated wood specimens as follows:

$$ASE (\%) = \frac{Su - Sm}{Su} X \ 100$$

Where Su and Sm are the volumetric swelling coefficients of unmodified sample and chemically modified wood sample respectively.

# Thermal conductivity measurements- Guarded Hot Plate Apparatus

**Guarded Hot Plate Apparatus:** A tangential board of 30x30x2.5 cm <sup>3</sup>(LxWxT), was prepared by joining 4 wood samples of 30x7.5x2.5 cm<sup>3</sup> (LxWXT) using tongue and groove joint to measure thermal conductivity as per IS:3346, 1980[9]. Two boards of each treatment were prepared and these samples were used between cold plate and the guarded hot plate. One wood board sample was placed in between hot plate and cold plate above the hot plate and other board was placed in between hot plate. In this method of measurement of thermal conductivity is based on the principle that the heat flows from guarded hot plate normal to the specimens to isothermal cold plate maintained at lower temperature [24]. Blotting paper was glued to edges of frame to cover open faces of the frame (figure 2).

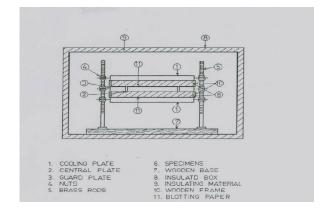


Figure 2: Guarded Hot Plate Apparatus[24]

Measurement of Thermal Conductivity: Thermocouples were used to control the power supplied to the guard heater to maintain the temperature balance between the centre and guard sections of the main heaters which are separated by a small gap. Thermocouples mounted in surface plates on either side of hot plates are used to measure the balanced conditions. The principle of measuring thermal conductivity is; the heat flow takes place normal to the specimen of unit thickness in unit time under steady state condition when the temperature difference across the two opposite surfaces of the sample is maintained as 1°C. Density of the control and chemically modified samples were determined before measurement of thermal conductivity. Two cold plates were kept above and below the upper specimen and bottom specimen respectively. The temperature of guard plate and central plate was raised by controlled supply of power and liquid was circulated at lower temperature to maintain temperature in cold plates at set point with the help of cryostat in which the liquid was maintained at lower temperature by compressor. When temperature of hot plate and cold plate reaches to the desired set temperatures, the set temperature of hot plate, was maintained by a temperature controller. A steady state of heat flow condition was achieved when the temperature of the guard plate, central plate, and cold plates becomes constant. The power consumption and temperature difference of hot plate and cold plates were measured and thermal conductivity is determined using:

 $K = Q \cdot d/A \cdot (\Theta h - \Theta c)$ 

Where ,K is the thermal conductivity (W/mK)

Q is rate of heat flow (W)

A is Area (sq. m)

 $\Theta_h$  is temperature of hot plate (°C)

 $\Theta_{c}$  is temperature of cold plate (°C)

d is thickness of sample (metre)

Q = VI

Where, Q is rate of heat flow (W)

- V- Voltage in Volt;
- I Current in Ampere

**Result and discussion** 

#### Weight Percent Gain (WPG)

The mean and standard error (SE) for weight percentage gains of the samples treated with propylene oxide and combination ofpropylene oxide- fyrol 51, with pyridine mixture for radial, tangential and volumetric directions are given below in figure 3. It was observed that the WPG for the present study was in similar range of 22.25- 34.39% as reported by previous study for Southern pine sapwood [20]. Radial and volumetric samples of *Pinusradiata* subjected to PF and PO treatment were insignificantly different from each other with WPG of 30.70  $\pm 0.82\%$  and 29.14  $\pm 0.62\%$  in radial direction; 31.45  $\pm 0.93\%$  and 30.16  $\pm 0.89\%$  in tangential direction. Whereas for tangential samples it was observed that PF had significantly more WPG of 30.50  $\pm 0.78\%$  from PO which had WPG 27.64  $\pm 0.88\%$ .

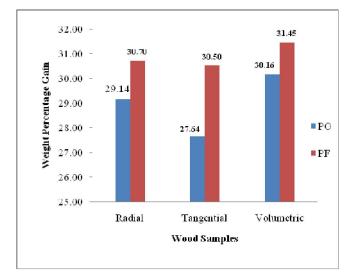


Figure 3: Weight Percentage Gain for PO and PF treatment

#### Water absorption

The mean and standard error (SE) for water absorption for all the treated samples for radial, tangential and volumetric samples were determined from 1hr to 336hrs or 14 days consisting of 17 absorption cycles. The results of treated and untreated samples are shown in figure 4. Treated and untreated samples showed increase in water absorption with time reaching almost constant uptake after sometime. As expected untreated or control samples absorbed more water than the modified wood samples. From the previous studies it has been established that the water accessible area decreases as the WPG increases. Modification cannot completely prevent water absorption, but reduce the absorption for longer period of time [11]. Untreated or Control radial samples had absorption percentage of 106.50 ±0.66%, 137.58 ±1.08% and 144.90 ±0.61% after 24hrs, 168hrs and 336hrs. PF had absorption of 45.77 ±1.16%, 74.33 ±0.90 and 79.41 ±0.96 % which was significantly different from by PO with absorption of 56.03 ±0.69%, 80.92 ±0.92% and 87.43 ±0.90% at 24hrs, 168hrs and 336hrs. Similarly for tangential samples control samples showed maximum absorption percentage of  $71.03 \pm 0.94\%$ , 132.20  $\pm 1.00\%$  and 142.53  $\pm 0.07\%$  after 24hrs, 168hrs and 336hrs. At 24hrs PF and PO showed insignificant difference in absorption with 39.39  $\pm$ 1.14% and 41.28  $\pm$ 0.62%. Whereas at 168hrs and 336hrs, PF had absorption of 69.22 ±0.90 and 76.26  $\pm 1.01$  % and which was insignificantly different from PO with 74.61 ±1.00% and 82.47 ±1.36% absorption respectively. Volumetric untreated samples after 24hrs, 168hrs and 336hrs had absorption percentage of  $61.01 \pm 0.69\%$ , 125.19 ±0.87% and 143.26 ±0.69%. PF treated samples had absorption of 30.50 ±0.67%, 64.35 ±0.80% and 75.49 ±0.77% at the mentioned time duration whereas PO had absorption percentage of 33.15± 0.38%, 65.98 ±0.89% and 82.51  $\pm 0.43\%$ . Absorption for PF was insignificantly different from PO at 24hrs and 336hrs whereas significantly different at 168hrs. The modified wood absorbed lower percentage of water as compared to control samples since capillary structures of wood are not blocked after modification, and modified wood may absorb water with in coarse capillary similar to untreated wood although less water enters cell wall affecting the overall absorption [25]. The present study also supports that with increase in time, the capillaries and void spaces becomes saturated with water, which increases the water absorption capacity [1]. The time taken for water uptake becomes constant at almost same time for treated and control samples as absorption becomes insignificantly different after 96-120hrs in radial direction for all the treatments including control but for tangential and volumetric samples the constant level of absorption was observed after 192-216hrs.

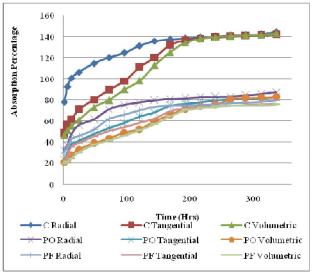


Figure 4: Absorption for PO and PF treatment

#### **Dimensional stability:**

#### Volumetric swelling coefficient

The effect of each treatment on swelling of wood was estimated. The mean and standard error (SE) for volumetric swelling coefficient (S) and Anti Swelling Efficiency (ASE) for different treatment were determined and are given in Table 2 and Table 3. S value for all the seven cycles were calculated and it was observed that all the treatment improved the volumetric swelling coefficient (S) as compared to the untreated or control samples. The control radial samples showed S value throughout the seven cycles ranging between 5.73  $\pm$ 0.26 to 7.16  $\pm$ 0.27. Among the treatments, PF treated radial samples showed insignificant difference of S value with PO treated samples as it ranged in between  $1.21 \pm 0.07$  to 2.25 $\pm 0.05$  for PF and 1.65  $\pm 0.07$  to 2.60  $\pm 0.10$  for PO. S value for untreated tangential samples ranged in between 6.41  $\pm 0.19$  to 7.84 ±0.18 for seven cycles. PF treatment indicated most effectiveness in lowering of swelling of wood as S value was in between 1.66  $\pm 0.05$  to 2.70  $\pm 0.06$  which was significantly different from PO treatment with S value ranging from 2.99  $\pm 0.04$  to 3.11  $\pm 0.06$  after 7<sup>th</sup> cycle. Similarly untreated wood samples had maximum S value ranging from 14.43 ±0.26 in 1<sup>st</sup> cycle to 16.25 ±0.33 after 7<sup>th</sup> cycle. [18]reported S value of 6-7.9 in four water soak cycles of Southern pine modified with propylene oxide with approximately 29% WPG. In this study PF and PO treatment showed better S values as reported [17]. S value among both the treatments throughout the seven cycles was 3.52  $\pm$ 0.07 to 5.20  $\pm$ 0.05 for PFtreatment and 4.35  $\pm 0.10$  to 6.06  $\pm 0.14$  for PO treatment, which were significantly different from each other.

the constant							
	Treatm ent	Direc tion	<b>S1</b>	<b>S2</b>	<b>S</b> 3	<b>S4</b>	<b>S</b> 5
	Untreat	Radial	5.73	6.17	6.50	6.63	6.78
		Tange ntial	6.41	6.75	6.98	7.22	7.49
	ed (C)	Volu metric	14.43	15.0	15.27	15.5	15.78
	Duranda	Radial	1.65	1.82	1.98	2.10	2.27
2	Propyle ne oxide	Tange ntial	2.07	2.29	2.43	2.63	2.79
	(PO)	Volu metric	4.35	4.80	5.10	5.37	5.54
	Propyle	Radial	1.21	1.41	1.64	1.82	1.95
	ne oxide	Tange ntial	1.66	1.82	1.99	2.24	2.40
00 Volumetric	and Fyrol51 (PF)	Volu metric	3.52	3.98	4.26	4.50	4.68
) Volumetric	Anti Swalling Efficiency						

Table 2: Volumetric Swelling coefficient for different treatment

**S6** 

6.96

7.72

16.01

2.42

2.97

5.87

2.08

2.58

4.99

**S7** 

7.16

7.84

16.25

2.60

3.11

6.06

2.25

2.70

5.20

## **Anti-Swelling Efficiency**

ASE of both the treatment is calculated from S values were relative to that of untreated samples. It is reported that with

increase in WPG, the ASE value increases up to about 35% WPG but after that WPG, the ASE reduces; this may be occurs as the WPG exceeds 35%, the volume of added chemical ruptures the cell wall [16, 21]. It was observed that ASE for PF was significantly different from PO in radial wood samples and it ranged between 78.87  $\pm 0.89\%$  to 68.28  $\pm 0.87\%$ for PF and 71.21 ±0.56% to 63.63 ±1.09% for PO. ASE calculated for tangential wood samples showed that PF treatment was significantly more effective in improving ASE with 73.98 ±0.89% and 65.45 ±0.62% after 1st and 7th cycle whereas PO had ASE from 67.74 ±0.96% to 60.20 ±0.99. As PF treatment resulted in lesser S value, this caused PF treated wood samples to have significantly higher ASE as compared to PO. PF treatment had ASE of 75.80 ±0.56% after 1<sup>st</sup> cycle and 67.92 ±0.62 % after 7th cycle whereas ASE for PO was  $69.84 \pm 0.70\%$  and  $62.64 \pm 0.84\%$  for the respective cycles. Chemical modification of Radiata pine by Propylene oxide-Triethyl amine (95/5 vol/vol) results in Weight percentage Gain of 32 to 34.2% with 67% of Anti Shrink Efficiency [14]. Similar result was observed for Southern pine with 29.2% of WPG when treated with propylene oxide resulted in ASE of 62- 50.3% after four cycles [21].

Table 3: Anti Swelling efficiency for PO and PF treatments

Treatm	Directi	ASE		ASE	ASE	ASE	ASE	ASE
ent	on	1	2	3	4	5	6	1
	Radial	71.2	70.3	69.4	68.2	66.4	65.0	63.63
Propyle	Kaulai	1	7	2	2	3	4	05.05
ne	Tangent	67.7	66.1	65.1	63.5	62.6	61.4	60.20
oxide	ial	4	0	4	5	2	8	60.20
(PO)	Volume	69.8	67.9	66.5	65.3	64.8	63.3	(2, (4
	tric	4	7	5	3	4	0	62.64
Propyle	Radial	78.8	76.9	74.5	72.3	71.0	69.8	68.28
ne	Radial	7	8	1	4	0	6	00.20
oxide	Tangent	73.9	72.8	71.4	68.9	67.9	66.4	65.45
and	ial	8	8	1	3	1	9	05.45
Fyrol51	Volume	75.8	73.4	72.0	70.9	70.2	68.7	67.92
(PF)	tric	0	2	2	1	4	4	07.92

# Thermal conductivity

Timber is a naturally insulating material and because of presence of air compartments within cellular structure creates a natural barrier to heat and cold. Lightweight timber is the best insulator increase as thermal conductivity increases with increase in density. Thermal conductivity also varies with moisture content, presence of the extractives and natural characteristics such as checks, knots and grain direction. Wood density depends on specific gravity and moisture content of wood. The maximum mean oven dried density for each board among the treatment was observed to be of PF with 683.93Kg/m<sup>3</sup>while PO had density of 678.57Kg/m<sup>3</sup>. It was observed that untreated or control board had oven dried density of 441.96 Kg/m<sup>3</sup> which is less than reported by [26] for small Radiata Pine sapwood samples of 465Kg/m<sup>3</sup> at 12% MC. The wood density also varies significantly within the growth for Radiata pine, with the early wood having lower density than the latewood. Early wood portion is higher close to pith therefore the average wood density is lower than that of the peripheral wood[8].

Major component of softwood are tracheids and trachieds formed early in a growing season have thin-wall cells with large diameters, whereas those formed later in the year are thick wall cells with small diameters. The thick walled latewood cells of tracheids are responsible for transfer of heat and mass. Heat is mainly transferred through cell walls by mode of conduction, and partially by convection of air in cell lumens[6].

Untreated samples resulted in maximum thermal conductivity for oven dried sample, of 0.076 w/mK, which is lower than as reported by in earlier study for P. radiataat 12% moisture content of 0.10- 0.14 w/mK [27]. [6] predicted thermal conductivity of Southern Yellow Pine and Scots Pine oven dried tangential wood samples with 20- 30% latewood to be in between 0.0788- 0.0837 w/mK and 0.0763- 0.0825 w/mK respectively. The oven-dried Douglas Fir had lower conductivity for wood of certain specific gravity, and concluded that there was some inherent properties of the wood affecting the conductivity [12]. In the present study propylene oxide reduced the conductivity but double step modification resulted in greater reduction as compared to single step modification as PF showed lower thermal conductivity value of 0.058 w/mK whereas PO treatment caused the conductivity to be 0.063 w/mK. Thermal resistivity is reciprocal of the thermal conductivity and is represented by "R value". In the present study it was observed that PF had maximum thermal resistivity of 17.241 K m/w followed by PO 15.873 K m/w while untreated sample had resistivity of 13.158 Km/w. Chemical modification with propylene oxide improves thermal property of wood and reduces thermal degradation. Addition of fire retardant Fyrol51 through double step modification further reduced thermal conductivity as organophosphorus compound improves thermal properties [14]. The improvement in thermal property of modified wood is comparable to some of commercial insulators like Insulating glass (0.084 W/mK), Vermiculite (0.069 W/mK), Silicon dioxide foam (0.055 W/mK) and Calcium silicate (0.051 W/mK)[24].

 Table 4: Density, Thermal conductivity and Thermal resistivity

 for oven dried samples

Sl. No.	Treatment type	Density (Kg/m <sup>3</sup> )	Thermal conductivity (k) (w/m K)	Thermal resistivity (R) (K m/w)
1.	Untreated (C)	441.96	0.076	13.158
2.	Propylene oxide (PO)	678.57	0.063	15.873
3.	Propylene oxide and Fyrol51(PF)	683.93	0.058	17.241

\*Density, Thermal conductivity, Thermal resistivity of Oven dried samples

#### Conclusion

Chemical modification of *P. radiata*using single and double step showed an evident increase in weight of wood. Water absorption of modified wood was much less than untreated wood. Dimensional stability also improved as the swelling coefficient for both the treatments were better when compared to control samples. Addition of fire retardant not only increased the Anti Swelling efficiency but also reduced the thermal conductivity. It can be suggested that wood modified by two step using Fyrol51 and Propylene oxide may be used as insulator in buildings. Further studies are required in this direction to substantiate the findings.

#### Acknowledgements

The authors are thankful to Director, Forest Research institute, Dehradun, India for providing the facilities. Authors are also thankful to the staff of Wood Preservation Discipline for providing necessary assistance.

#### References

- Devi, R.R. and T.K. Maji. Chemical modification of Semul with styrene acrylonitrile co-polymer and organically modified nanoclay. *Wood Science Technology*, 2012, 46:299-315.
- [2] Donath, S., H. Militz, and C. Mai. Wood modification with alcoxysilanes. *Wood Science Technology*, 2004, 38:555-566.
- [3] Ellis W. D and Rowell R. M. Reaction of isocyanates with southern pine wood to improve dimensional stability and decay resistance. *Wood and Fiber Science*, 1984, 16(3): 349-356.
- [4] Ellis, W. D., and Rowell, R. M. Flame-retardant treatment of wood with a diisocyanate and an oligomerphosphate, *Wood Fiber Sci.* 21(4), 367-375, 1989.
- [5] Forest Products Laboratory. Wood handbook—Wood as an engineering material. *General Technical Report FPL-GTR-190*, Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 2010,508 p.
- [6] Gu, H M, Zink-Sharp, A. Geometric model for softwood transverse thermal conductivity. Part i. Wood and Fiber Science, 2005, 37(4): 699 – 711.
- [7] Hansmann, C., G. Weichslberger, and W. Gindl. A two-step modification treatment of solid wood by bulk modification and surface treatment. *Wood Science Technology*, 2005, 39:502-511.
- [8] Herritsch, A. Investigations on Wood Stability and Related Properties of Radiata Pine. Doctor of Philosophy in Chemical Engineering, Department of Chemical and Process Engineering, University of Canterbury, New Zealand, 2007.
- [9] IS: 3346. *Method for determination of thermal conductivity of thermal insulation material.* BIS, 1980.
- [10] Kollmann, F.F.P., Côté, W. A. Principles of wood science and technology. Pensumtjeneste. Oslo, 1995, 592pp.
- [11] Lahtela, V., Hämäläinen, K and Kärki, T. The effects of preservatives on the properties of wood after modification (review paper). *Baltic Forestry*, 2014, 20 (1):189-203.

- [12] MacLean, J.D. Thermal conductivity of wood. *Heating, piping and air conditioning*, 1941, 13(6): 380-391.
- [13] Pandey, K.K., Jayashree and , H.C. Nagaveni. Study of dimensional stability, decay resistance and light stability of Phenylisothiocynate modified Rubberwood. *Bio resources*, 2009, 4(1): 257-267.
- [14] Rowell, R. M, R. A. Susott, W. F. DeGroot and F. Shafzadeh. Bonding fire retardants to wood. Part I. Thermal behavior of chemical bonding agents. *Wood Fiber Science*, 1984, 6(2): 214-223.
- [15] Rowell, R. M. and Banks, W.B. Water repellency and dimensional stability of wood. USDA *Forest Service General Technical Report FPL 50*, Forest Products Laboratory, Madison, WI, 1985.
- [16] Rowell, R.M. and Ellis, W.D. Determination of dimensional stabilization of wood using the water-soak method. *Wood and Fibe*, r1978, 10(2):104–111.
- [17] Rowell, R.M. and Ellis, W.D. Effects of moisture on the chemical modification of wood with epoxides and isocyanates. *Wood and Fiber Sci.* 1984b, 16(2):257–276.
- [18] Rowell, R.M. and Ellis, W.D. Reaction of Epoxides with wood. *Research paper FPL-451*. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 1984a.
- [19] Rowell, R.M. Chemical modification of wood. *Forest Product Abstracts*, 1983, 6(12): 363-382.
- [20] Rowell, R.M. Chemical modification of wood: Reactions of alkylene oxides with southern yellow pine. *Wood Science*, 1975, 7(3):240–246.
- [21] Rowell, R.M.. Chemical modification of wood. Handbook of wood chemistry and wood composite. CRC Press, 2005, 381-420.
- [22] Rowell, Roger M.; Banks, W. Bart. Water repellency and dimensional stability of wood. *Gen. Tech. Rep. FPL-50*. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 1985, 24 p.
- [23] Siau, J.F. Transport processes in wood. Springer-Verlag, Heidelberg, 1984.
- [24] Suman B.M.Thermal conductivity measurement of powder material and its optimum application for energy efficient cold storage. *International Journal of Applied Engineering and Technology*. 2015, Vol. 5 (1): 78-83.
- [25] Tarkow, H and Stam, A. J. Acetylated wood.*Aircraft design*, *FPL*. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 1955.
- [26] Turner, J., Riley, S., Haque, N., and Cown, D. Comparison of the water absorbency of Douglas-fir and radiata pine framing timber NZ Douglas-fir Cooperative Report No. 47, August 2005.
- [27] Buchanan, A. H. Information sheet thermal.www.nzwood.co.nz/wpcontent/uploads/2013/06/rvalue.pdf. 2013.