A study on Flame-retardancy Property of UV Curable Epoxy Coating for Wooden Surfaces using Boron Diluent and Phosphorus Based Initiator

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ABSTRACT

In the present paper,boron based diluent was synthesized and incorporated in to a Ultraviolet (UV) radiation curable epoxy coating composition comprising of phosphorus based initiator (Trimethylbenzoyl diphenyl phosphine oxide) for enhancing its flame retardant property. The boron based diluent was synthesized by thermal polymerization technique. The presence of boron and phosphorus on the coating surface was confirmed by Energy Dispersive X-Ray (EDX) and X-ray photoelectron spectroscopy (XPS) techniques and functionality was determination by Fourier Transform Infra-Red (FTIR) and proton/boron NMR spectroscopy technique. The flame retardency property of the coating composition was confirmed by determining limiting oxygen index,vertical burning test, rate of burning. Results revealed that the incorporation of boron diluent increases the Limiting Oxygen Index value from 21% to 33% and decreases the rate of burning from 58 to 6 seconds. The char yield confirms the self-extinguishing property of the coating system.

KEYWORDS: *UV radiation, Flame retardant, Epoxy based wood coating, Boron diluent, Phosphorus Initiator.*

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1. INTRODUCTION

Now a days UV curable coatings are preferred over solvent based coating systems for wooden surface due to their environment friendly nature [1-3]. UV curable coatings require no solvent and are considered safe for the environment[4-5] whereas the solvent based coatings release hazardous organic solvents[6]. UV curable coatings give good aesthetic, chemical and mechanical properties to the wooden surfaces and thus are being preferred[7].

The recent global trends of organic coating industries are mostly focused on sustainability and environment friendly coatings like water-based and high solids coating for wood protection. The UV-cured coatings are based on 100% a solid, which means that the entire coating applied on wood surface gets cured on exposure to UV rays and turns into a solid coating without release of any solvents. The curing process is instantaneous on exposure to UV radiation leading to drying of coating on surface where it is applied and the coated product is ready to be handled or stored. In case of conventional coatings, organic solvent acts as a carrier of coating material such as shellac, melamine, polyurethane, etc. The organic solvents evaporate off from the wet coated surface leaving behind a coating. Multiple coats need to be applied and the drying process takes about 6-7 hours for each coat.

Wood is used traditionally in furniture, handicrafts and also for construction applications due to its unique features but it is highly susceptible to fire or flame. Hence, flame retardancy of into coatings applied on wood, will be a highly useful property. In conventional thermally cured solvent-borne coating system, inorganic additives may be used for adding flame retardant property,[8] but in UV curable coating compositions the inorganic flame retardant additives are usually incompatible[9]. According to standard protocol, a coating system must possess a limiting oxygen index (LOI) of 21 to be called flame retardant.

UV curing technique has been used for industrial fire retardant coating applications by adding nano silicon oxide and nano composite coating additives as flame retardants[10]. The additive here does not form a part of crosslinked coating structure but remains mixed in the coating composition. Saket mulge et al., [11] have described a method for synthesis of a phosphorus containing flame retardant having UV curing properties for coating application. The addition of this agent enhanced the LOI of the coating system to 27% but the coating composition is highly viscous and thus not sprayable. A method[12] has been described to synthesize silicon containing hyper-branched polyphosphonate acrylate diluent to increase flame retardancy of epoxy acrylate based UV-curable coating composition. It was observed that although both thermal stability and char yield increases with increase in concentration of silicon based phosphonate acrylate in coating system but in burning test (UL 94), none of the samples had V0 rating. Lijuan Chen et al.,[13] synthesized a new intumescent flame retardant containing both phosphorus and nitrogen and incorporated it into epoxy acrylate resin in different ratio. The degradation pattern of epoxy acrylate containing these reagent suggests that its addition enhances the char residue. H. Liang, et al.,[14] described a process to synthesize methacrylated phenolic melamine as a flame retardant multifunctional oligomer for

UV curable coatings. The LOI value was found to increase from 21.5% to 26.5%. A series of hyperbranched polyphosphate acrylates (HPPAs) were prepared by the reaction of tri(acryloyloxyethyl) phosphate (TAEP) with piperazine. HPPA was blended with TAEP in different ratios to obtain a series of flame retardant UV curable resins but in this case TAEP is active as flame retardant in gas phase [16]. Durva naik, et al.,[17] have studied the synergistic behavior of silicon and phosphorus in flame retardant UV coatings but LOI value was observed 24% only. The diacrylate reactive diluent was synthesized by reacting glycidyl methacrylate, piperazine, and cyclic ethylene chlorophosphate. The synthesized reactive diluent was utilized to formulate UV-curable wood coating. The UV cured coatings films were evaluated for their flame retardant performance, optical properties and solvent resistance property.

The use of inorganic boron based compounds has been described[18-19] for use in UV curable coatings as flame retardants.

The present study describes synthesis of boron based reactive diluent for use in flame retardant UV curable coating is applied on wooden substrates. The synthesized boron diluent was mixed with UV curable epoxy and phosphorus initiator based coating. The effect of its addition on flame retardancy property of the coating composition has been studied along with other physiochemical and thermal properties.

2. EXPERIMENTAL

2.1 Raw Materials for Coating Composition

Sheesham wood formed into small blocks was supplied by local market Delhi, Epoxy acrylate resin (EA) (Mol. wt. 520, viscosity 4000 cps@ 60°C), Trimethylol propane triacrylate (TMTA) (Mol.wt 428, viscosity 65 cps@25°C), Tripropylene glycol diacrylate (TPGDA) (M.wt. 300, viscosity 15 cps@25°C), Dipentaerythritol penta acrylate (DPPA) (M.wt. 524, viscosity 6600 cps@25°C) were supplied by Miwon Commercial Co. Ltd. and Trimethylbenzoyl diphenyl phosphine oxide (TPO) photo initiator (Mol.wt. 348, purity 97% yellow powder) was supplied by Rhan Corp. These materials were used as obtained from the suppliers for the preparation of coating composition.

2.2 Raw Materials for Boron Diluent Synthesis

Phenyl boric acid (PBA), Glycidyl methacrylate (GMA), Triethylamine (TEA), Sulphamic acid and Tetrahydrofuran (THF) were obtained from S.D Fine Chemicals in LR grade and were used for the synthesis of boron based diluent.

2.3 Method for Synthesis of Boron based Reactive Diluent

The glycidyl methacrylate (0.326 mole), sulphamic acid (0.0164 mole) and 100 mL of tetrahydrofuran were mixed and stirred continuously till a homogeneous solution was obtained. Phenyl boric acid (0.205 mole) was mixed with triethylamine (0.0024 mole) separately and this mixture was added. The reaction was carried out at 30°C for 24 hours. After completion of the reaction, solution was filtered. The solvent was removed using rotatory vacuum evaporator and light yellow viscous product was collected. The reaction taking place during synthesis of boron acrylate reactive diluent is depicted in Figure 1. Triethylamine aids in the opening of oxirane ring in glycidyl methacrylate leading to reaction of phenyl boric acid with glycidyl methacrylate.

2.4 Preparation of UV Curable Coating Composition

The synthesized boron based diluent was mixed in UV-curable coating compositions in varying amount (0 to 6.2% by weight), while keeping the amounts of epoxy resin, photoinitiator (TPO) and other reactive diluents constant (Table 1). Each composition was thoroughly mixed to make it homogeneous. The prepared compositions were applied on wooden sample (10 × 12 cm) by spray technique. The wet coated wooden sample was cured by exposing the sample to UV radiation at 365 nm wavelength (UV lamp 300 W/inch) with the

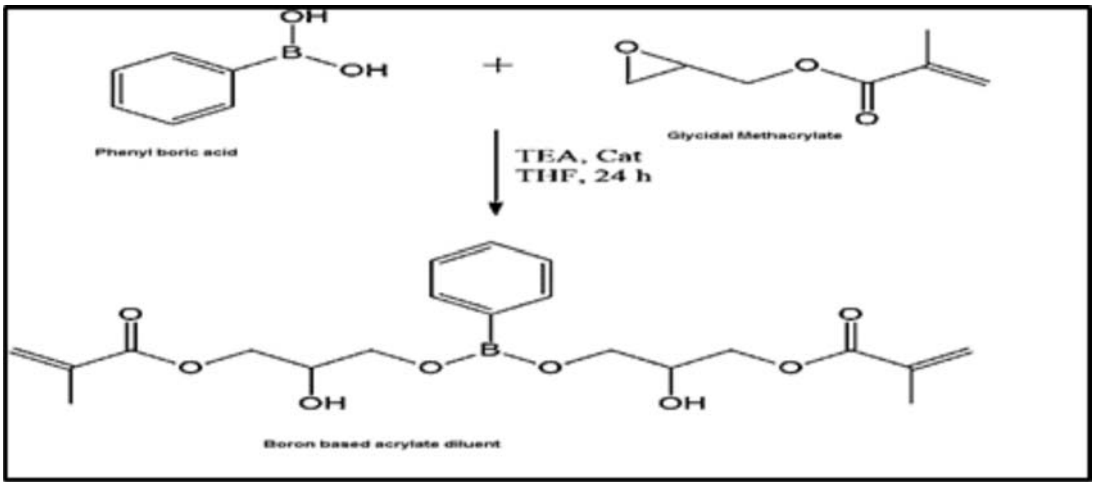

Figure 1. Synthesis of boron based diluent

distance between sample and lamp of 10 cm. The exposure time given was 10 seconds and the dry coating thickness was measured as 40 to 45 μm.

3. CHARACTERIZATION

The coating compositions were kept in dark coloured tightly closed containers and were stored away from heat and light. The coated and cured specimens were wrapped in plastic films after UV exposure. Each test specimen was conditioned as per the conditioning procedure given in the standard protocol followed for the particular test. The number of specimen tested for each technique were different. In case of LOI, UL 94 vertical burning test, rate of burning, the number of specimens for each test were 10. The results reported are average of 10 readings and the error is ± 0.5. For Gloss, dry heat, steam, stain and pencil hardness tests, 2 specimens were used for each test.

TABLE 1. UV curable Coating compositions prepared using boron diluent

Oligomer (g)	**Reactive Diluents (g)**			**Boron Diluent (g)**	**Initiator (g)**
EA	**DPPA**	**TMTA**	**TPGDA**		**TPO**
80	10	30	250	0	7
80	10	30	250	5	7
80	10	30	250	10	7
80	10	30	250	15	7
80	10	30	250	20	7
80	10	30	250	25	7

^{1}H NMR analysis was performed using Bruker ADVANCE III 500 MHz (AV 500). Tetramethyl Silane (TMS) was taken as internal standard and $CDCl_3$ as solvent. ^{11}B proton NMR was performed using Jeol ECX400 MHz multinuclear probe.

The FTIR spectroscopic analysis was performed using Shimadzu (IR Affinity-1S, Japan).

X-ray photoelectron analysis was performed using Physical Electronics PHI 5000 Versa Probe III. The executing conditions are: monochromatic Alfa source of energy = 14.86.7 eV, pass energy = 280 eV for survey scan to investigate the surface chemistry of prepared coating.

Energy dispersive X-ray spectroscopy (EDX) was performed using Broker XFlash detector 630 M in house.

The evaluation of flame retardancy[10] properties carried out in the study are on coated wooden substrates.

Limiting oxygen index is a test to determine the minimum oxygen level required for combustibility of a material. LOI was determined as per standard ASTM D2863.

Vertical burning test was performed to determine the flame retardancy of coating. The test samples 127 mm × 12 mm × 2 mm were suspended vertically and ignited by LPG burner to study the spread ability of flame.

The horizontal burning rate of UV coated sample was determined by using the standard test method ASTM D 635. The sample of size 125 × 13 × 10 mm was held horizontally by holder and free edge of the test sample was exposed to the flame upto the length of 2 cm for 30 s at room temperature. The ignition source was removed and then the combustion behavior of the specimen was studied.

Thermo gravimetric analysis (TA Instrument) of UV cured film was carried out keeping heating @ 5°C/min.

Viscosity of the coating compositions were measured with Brookfield viscometer (DV-II+ Pro) using spindle no. S4 @ 25°C.

After curing the coating composition, 40-50 mg cured film was subjected to soxhlet extraction for 24 hours in methyl ethyl ketone (MEK) solvent. After extraction, the sample was vacuum dryed at 60°C for 12 hours till constant weight was achieved. The gel content was determined using the formula:

$$\text{Gel Fraction (\%)} = \frac{W_t}{W_0} \times 100$$

Where, W_0 is the original weight and Wt is the weight after extraction and drying.

Gloss of coated wooden sample was determined as per ASTM D: 2457-90 by Novo gloss meter.

The steam resistance property was measured as per EN: 438 - 2, 1991.

Dry heat resistance was measured as per EN 438 – 2: 1991.

Pencil hardness test was evaluated as per ASTM: D 3363. The UV coated wooden sample of size (250 × 50 ×10 mm) were used for study.

Stain resistance was determined as per EN – 438 – 2: 1991.

The adhesion of coating on wood surface was evaluated as per ISO 2409: 2013 (E).

4. RESULTS AND DISCUSSION

4.1 NMR Analysis of Synthesized Boron based Diluent

As per the ^{1}H NMR spectrum (Fig. 2) five integrated protons occur at the chemical shift of 7.36–7.99 ppm, which corresponds to the aromatic region proton of the boron diacrylate. The olefinic protons from acrylate moiety appear as doublet at 6.07-6.00 ppm. Hydroxy proton occurs as a doublet at 5.64 and 5.25 ppm. Protons between the hydroxyl group and carbonyl appear at 4.47 ppm[2].

As per the ^{11}B NMR characteristic singlet peak occurs at 26.52 ppm corresponding to the alkyl boronates absorption -C-B-O- linkage (Fig. 3).

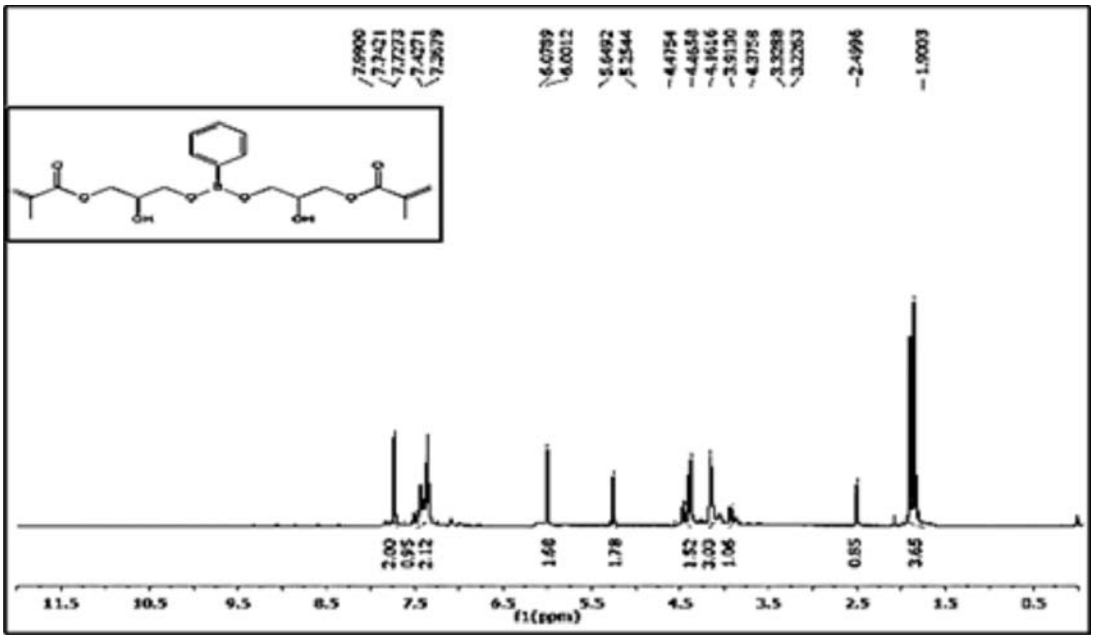

Figure 2: ^{1}H NMR spectra of Boron based diluent

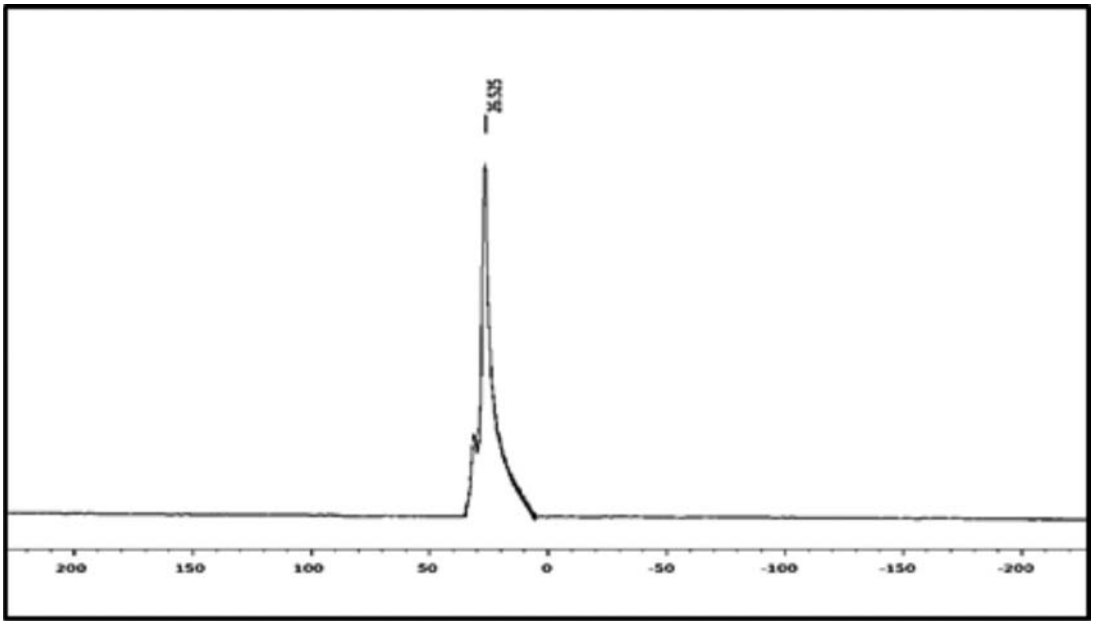

Figure 3: ^{11}B NMR spectra of Boron based reactive diluent

4.2 FTIR Analysis of Synthesized Boron based Diluent

IR spectra (Fig. 4) of synthesized boron based diluent shows characteristic peaks of (C-H) aliphatic stretching bands at 2963 cm^{-1}. The strong absorption band around 1712 cm^{-1} corresponds to the carbonyl group (-C=O), the broad peak at 3404 cm^{-1} is of hydroxyl functionality (-OH). The (-C-O) absorption peak at 1163 cm^{-1} is found intact in boron acrylate. The peaks at 1307 and 646 cm^{-1} confirm the formation of (B-O-C) and (-B-C-) bond indicated by their stretching peaks. The C-C stretch of aromatic ring of PBA are seen at 1634 cm^{-1} and 1442 cm^{-1}.

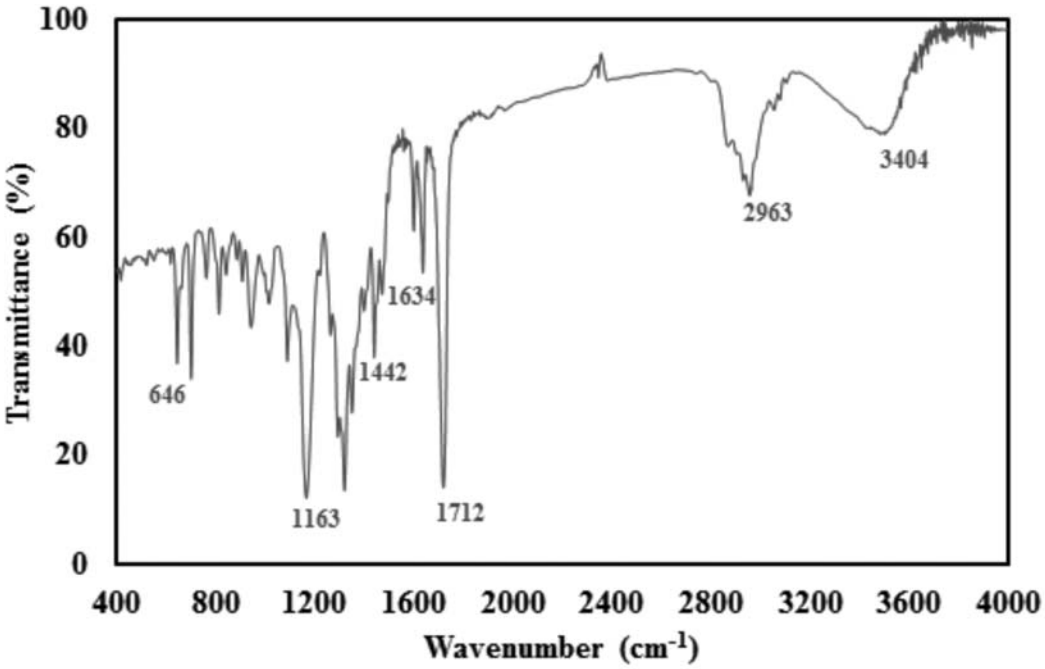

Figure 4: FTIR spectra of Boron based diluent

4.3 FTIR Spectra of Boron and Phosphorus based UV Curable Coating Composition

FTIR spectra (Fig. 5) of boron diluent and phosphorus initiator based coating composition shows characteristic -C-O deformation bands of bisphenol A type epoxy resin observed at 915 cm^{-1}. The broad band at 3437 cm^{-1} is assigned to O-H stretching of hydroxyl group,-C=C at 1604 cm^{-1}, -C=O at 1723 cm-1 and -CH at 2927 cm^{-1} indicate the presence of double bonds and carbonyl group. The strong absorption around 1717 cm^{-1} corresponds to the vibration of C=O group. The presence of acrylate group is confirmed by the absorption bands observed at 1637 and 811 cm^{-1}. The

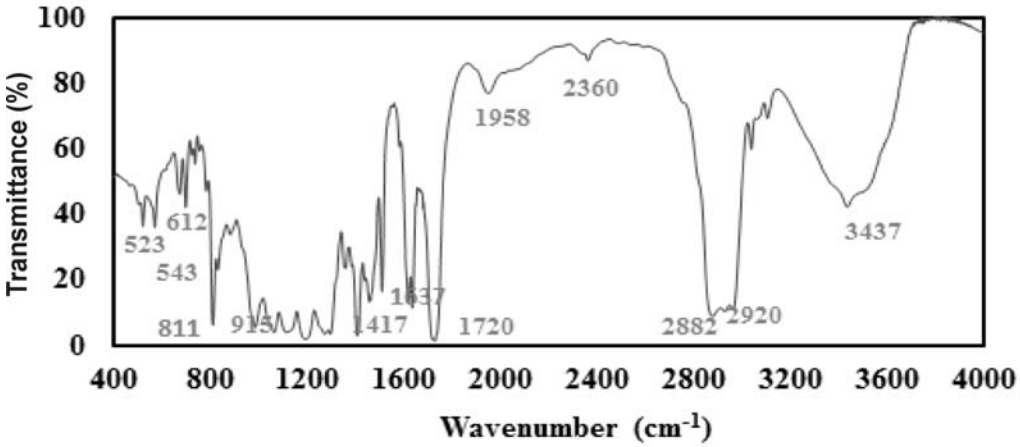

Figure 5: FTIR spectra of flame retardant coating composition after curing

absorption band at 1417 cm^{-1} indicates B-O group in the cyclic borate ester.

4.4 XPS and EDX Analysis for Boron and Phosphorous Group Present on Coating Surface

The binding energy of boron element was determined by the XPS analysis. The boron are usually oxidized at the surface of coating when boron is implanted in oxide, the strong B2O3 overlaps the B1s region and binding energy peak of 189.45 eV show that boron element is available on the surface of coating composition (Fig. 6) and EDX spectra confirmed the phosphorus group also present on coating surface in (Fig. 7).

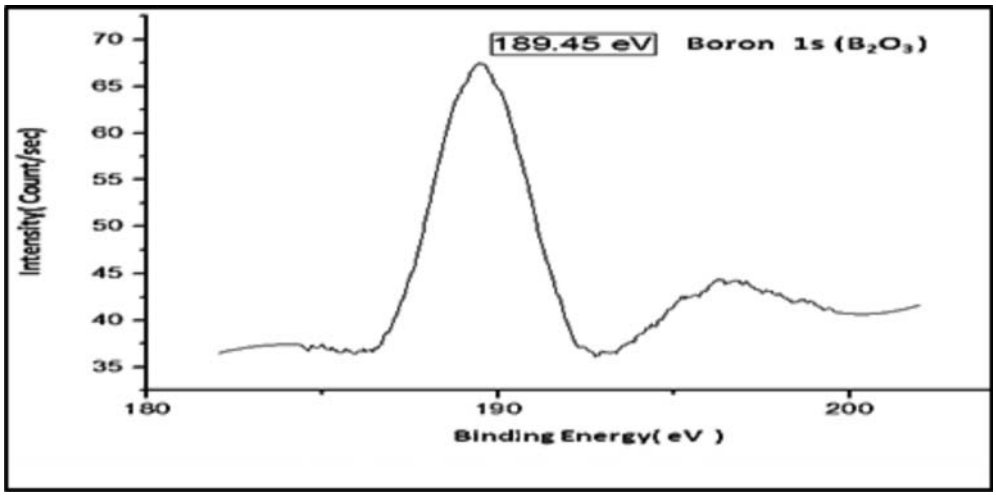

Figure 6. X-ray photoelectron spectroscopy spectra for boron confirmed on coating surface

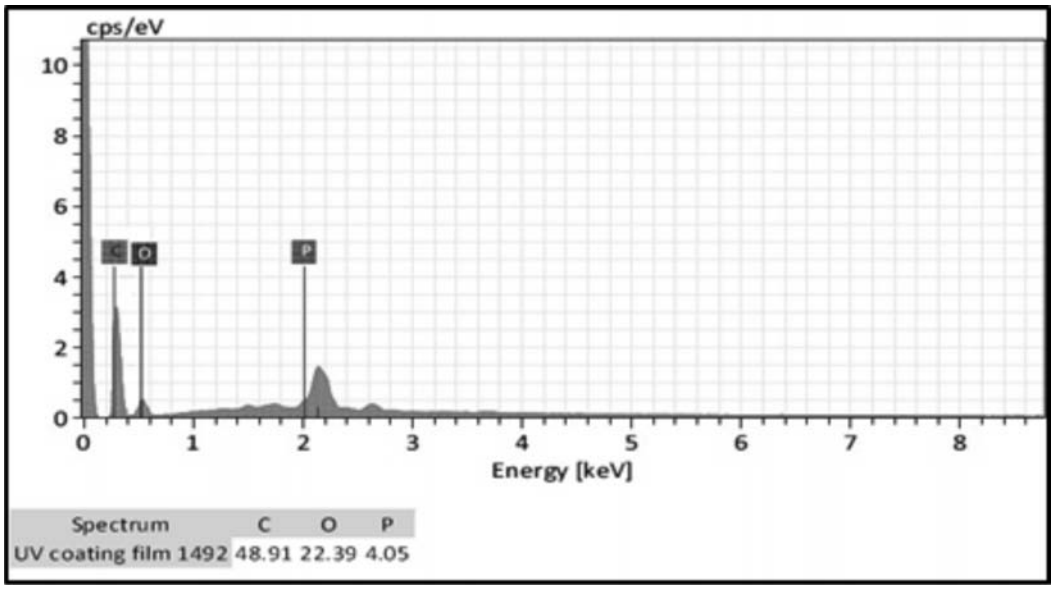

Figure 7. EDX spectra for phosphorus confirmed on coating surface

4.5 Flame Retardency Property

4.5.1 Limiting oxygen index (LOI)

With incorporation of boron based diluent, the LOI of the coating system increased from 21% to 33%. As the concentration of boron based diluent was increased, LOI shows a gradual increase in value upto 20 g, and thereafter no significant increase was observed (Fig. 8). The increase in flame retardancy with increased concentration was due to the generation of more amount of boron oxide which formed upon the pyrolysis of (B-C) and (B-O-C) bonds during the process of combustion which helps in the formation of more amounts of residual char which act as a protective barrier against the fire. The residual char formation increase the decomposition temperature of epoxy oligomer by preventing the heat transfer from source to the polymeric material.

4.5.2 Thermo gravimetric analysis (TGA)

In TGA the first thermal degradation at 350°C temperature occurs due to the decomposition of uncross-linked part in polymer backbone, and second degradation at 500°C temperature is assigned to the cross-linked three-dimensional network structure shown in Figure 9. Thermal stability mainly concerns with the release of decomposition products in the form of residual char given in Table 2. As the boron content in the composition is increased, the thermal stability of the UV coating formulations also increases. The higher char yield is attributed to the flame retardant property of organo-boron reactive diluent and phosphorus initiator. The flame retardancy was originated by the formation of a non-penetrable surface of boron oxide and phosphorus oxide during degradation of cross-linked polymeric substrate. It means

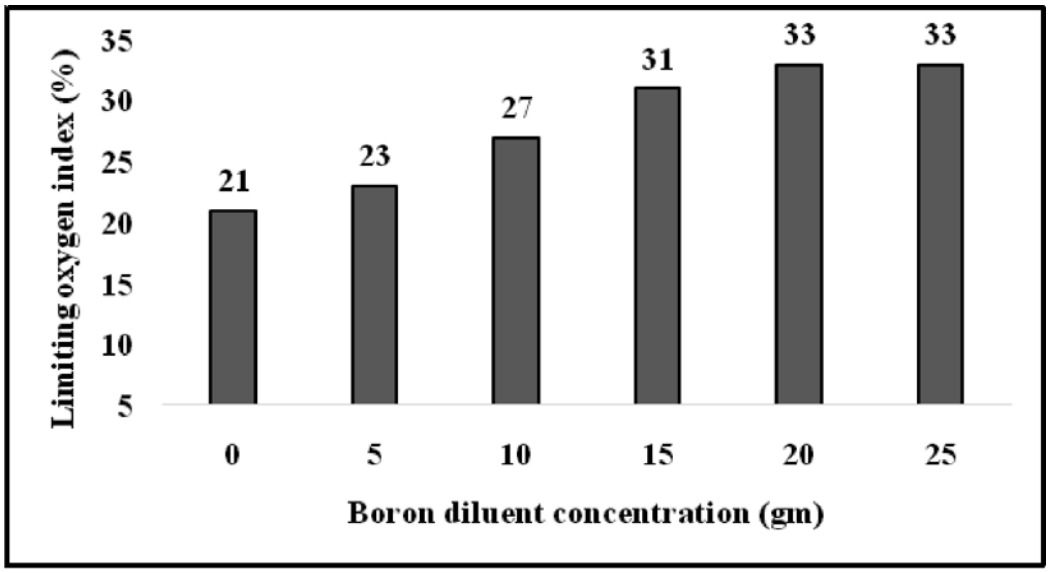

Figure 8: LOI results of Phosphorus initiator and boron diluent based coating composition

that, during the process of combustion, boronic and phosphoric acid losses water molecule in the system and HBO2 transforms to the boron oxide (B2O3) and HPO2 transform the PO2+ H2O, which formed glassy surface to provide a thermal protective barrier.

4.5.3 Vertical burning test UL-94

Flame retardant based UV coating samples were tested for combustion by subjecting them to burning time of 10 seconds using burner flame. After that the flame was removed to check the flame spread behavior of sample.

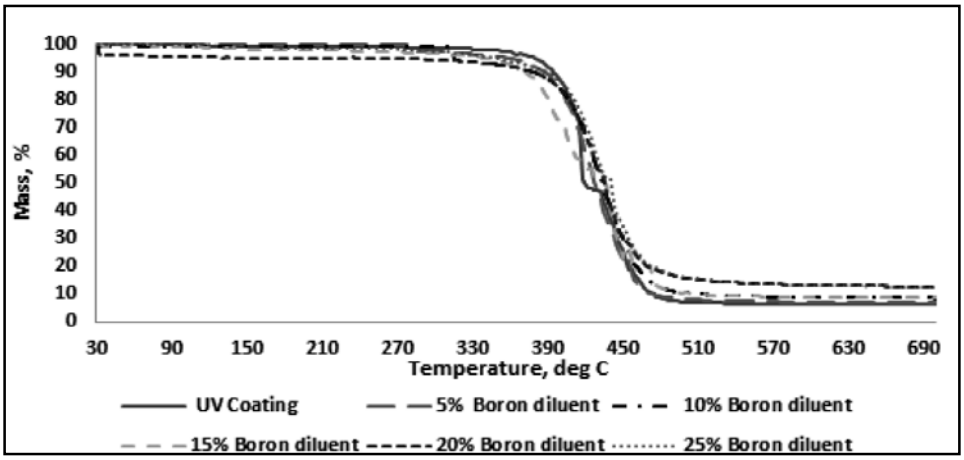

Figure 9. TGA analysis curve of coating compositions

TABLE 2. Char yield obtained after TGA of UV coatings

UV Coating Compositions	Char Yield (%) @700 (°C)
Coating 0 gm diluent	6.3
Coating 5 gm boron diluent	6.9
Coating 10 gm boron diluent	8.4
Coating 15 gm boron diluent	8.8
Coating 20 gm boron diluent	12.84
Coating 25 gm boron diluent	12.86

As can be seen from (Fig. 10). The incorporation of boron diluent enhances the self-extinguishing property of the coating. The dripping char residue was not observed in the samples and also with increase in boron based diluent concentration, the flame spread ability got decreased. Dripping is not taking place as the sample is wooden in nature and coating applied on wooden substrate is under study. Thus, it can be seen that the boron diluent and phosphorus initiator act as a good flame retardant in UV curable epoxy based coating. The amount of 20 g of boron diluent was found optimum for imparting the desired flame retardency property in the coating composition as the time of burning in case of coating compositions having 20 g and 25 g boron diluent was less than 10 seconds, which means V0 rating.

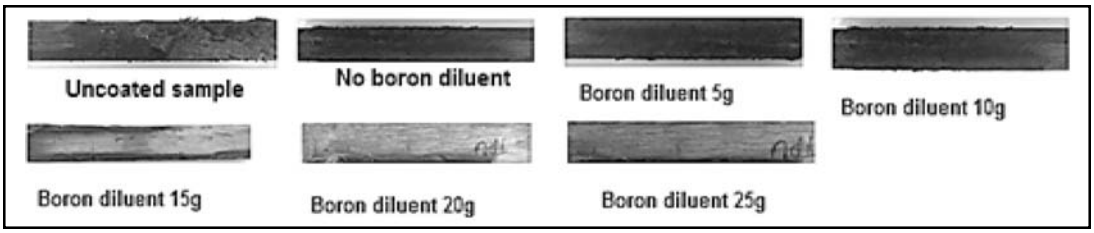

Figure 10. Effect of boron diluent on vertical burning test spread of wooden sample

TABLE 3. Results on rate of burning

S. No.	Samples	Burn Time (s)	Burn Length (mm)
1	Uncoated	58	100
2	Coated, 0% diluent	28	70
3	Coated, 5% boron diluent	21	18
4	Coated, 10% boron diluent	14	14
5	Coated, 15% boron diluent	10	10
6	Coated, 20% boron diluent	6	8
7	Coated, 25% boron diluent	6	8

4.5.4 Rate of burning test (ASTM D 635)

Table 3 shows that the burning rate decreases with the increase in boron diluent concentration which shows that the boron diluent play an important role in imparting flame retardant property.

4.6 Effect of Boron based Diluent on Other Physico-mechanical and Chemical Properties of Coating Compositions

The physico-mechanical and chemical properties of the coating composition with 20 gm boron diluent were also analyzed to study the effect of boron based diluent on these properties (Table 4).

Viscosity is one of the important parameters for any coating application. Incorporation of boron diluent in the coating composition does not affect its viscosity and spray ability. The gel content was determined for cured coating compositions with and without boron diluent. No change in gel content was observed on addition of boron diluent. The value of gel content was found to be 98% in both cases. Gloss is the key parameter of the coating composition for aesthetic acceptance by the consumer, and no effect of boron diluent was observed on gloss. No effect of steam or dry heat could be seen on the surface of all the wooden samples indicating formation of good crosslink network obtained between resin and

TABLE 4. Viscosity, Gel content, Gloss, Steam, Dry heat, Pencil hardness, Stain resistance and cross cut adhesion of UV coated wooden sample

Property Profile	UV Coating Composition	
	Without boron diluent	With boron diluent (20gm)
Viscosity (cP)	92	90
Gel Content (%)	98	98
Gloss (%)	79	81
Steam Resistance	No change	No change
Dry Heat	Not Affected	Not Affected
Pencil Hardness	HB	HB
Stain Resistance	No Staining	No Staining
Cross cut Adhesion	'0' coating does not get detached at all.	'0' coating does not get detached at all.

diluents (Table 4). All UV coated wood samples showed HB level of pencil hardness which means that there was no adverse effect of boron diluent on surface hardness of UV coated samples. UV cured wooden samples (with and without boron diluent) exhibited no staining of caustic and acetone. Adhesion property measured as Cross Cut adhesion was found to be unaffected by addition of boron diluent. Thus, no adverse effect on the physico-mechanical and chemical properties was observed.

CONCLUSION

In this study, boron based diluent was synthesized and characterized. The incorporation of boron diluent in the coating composition increases its LOI from 21% to 33% and rate of burning decreased from 58 to 6 seconds. The original physiochemical properties (e.g., gel content, viscosity, gloss, stain, pencil hardness etc.) of the coating composition remained unaffected by incorporation of boron diluent. The vertical burning test and char yield confirm the self-extinguishing property of the system with incorporation of boron diluent. Thus it can be concluded that boron diluent can act as good flame retardant additive to UV curable epoxy based coating for wooden surfaces.

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REFERENCES

1. Q. Wu, Y. Hu, et al, "High-performance soybean-oil-based epoxy acrylate resins: "green" synthesis and application in UV-curable coatings" *ACS Sustain. Chem. Eng.* 6 (2018) 8340-8349.
2. G. Phalak, D. Patil, et al, "Development of tri-functional biobased reactive diluent from ricinoleic acid for UV curable coating application" *Ind. Crops Prod.* 119 (2018) 9-21.
3. K.M. Idriss Ali et al. "Ultraviolet Curing of Epoxy Coating on Wood Surface" Radiation and Polymer Chemistry Laboratory, Institute of Nuclear Science and Technology, *Bangladesh Atomic Energy Commission,* 4 June 1997.
4. Andrew A.Sokol "Ultraviolet (UV) cured coatings" *Metal Finishing,* 108, (2010), 196-204.
5. Kinga Orwat, Pawe? Bernard "Traditional vs. UV-Cured coatings - an inquiry-based experiment for introducing green chemistry" Macedonian *Journal of Chemistry and Chemical Engineering,* 37(2), 215-224.
6. Zhishi Guo, John C.S. Chang "Estimation of the rate of VOC emissions from solvent-based indoor coating materials based on product formulation" *Atmospheric Environment,* 33 (1999) 1205-1215.
7. Rajkumar Singh Rawat, "UV coatings for wooden surfaces" *Progress in Organic Coatings,* 135, (2019), 490-495.
8. H. Abd El-Wahab, M. Abd El-Fattah "Preparation and characterization of flame retardant solvent base and emulsion paints" *Progress in Organic Coatings,* 69, (2010), 272-277.
9. ThRandoux, HVan den Bergen "Halogen-free flame retardant radiation curable coatings" *Progress in Organic Coatings,* 45 (2002), 281-289
10. Laura Anne Lowden et.al "Flammability behaviour of wood and a review of the methods for its reduction" *Fire Sci Rev* 2, 4 (2013).
11. Saket Mulge, Siddhesh Mestry, "Phosphorus-containing reactive agent for UV-curable flame-retardant wood coating" *J. of Coating Technology Research,* 16 (11), 2019.
12. Xiaofeng Wang , Jing Zhan, "Flame Retardancy and Thermal Properties of Novel UV-Curable Epoxy Acrylate Coatings Modified by a Silicon-Bearing Hyperbranched Polyphosphonate Acrylate" *Ind. Eng. Chem. Res.* 52 (2013), 5548-5555.
13. Lijuan Chen , Lei Song "A new intumescent flame retardant containing phosphorus and nitrogen: Preparation, thermal properties and application to UV curable coating" *Progress in Organic Coatings,* 70, (2011), 59-66.
14. H. Liang, A. Asif, W. Shi, Thermal degradation and flame retardancy of a novel methacrylated phenolic melamine used for UV curable flame retardant coatings, *Polym. Degrad. Stab.* 87 (2005) 495-501.

15. Z. Huang, W. Shi, Synthesis and properties of a novel hyperbranched polyphosphate acrylate applied to UV curable flame retardant coatings, *Eur. Polymer J.* 43 (2007) 1302-1312.

16. Durva Naik, Kunal Wazark et al, "UV-curable flame-retardant coatings based on phosphorous and silicon containing oligomers", *J. Coat. Technol. Res,* 16 (3), (2019) 733-743.

17. Gunawant Lokhande et al "Synthesis and properties of phosphate based diacrylate reactive diluent applied to UV-curable flame retardant wood coating", *Journal of Coatings Technology and Research,* 14(1), 2016.

18. Mehmet Dogan et al, "Flame retardant effect of boron compounds in polymeric materials" Composites Part B, Engineering Volume 222, (2021), 109088.

19. Tuba Cakır Canak et al. "Boron containing UV-curable epoxy acrylate coatings" Progress in Organic Coatings, Volume 77, (2014) 1911-1918.

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