



## Treatment of plywood from burning by synthesis a new protective coating through sol-gel

A. A. Younis

Fire and Explosion Protection (FEP), National Institute for Standards (NIS), Giza, Egypt.

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### ABSTRACT

Approximately 750,000 multi-family housing units experienced roofing problems due to fire-retardant-treated (FRT) plywood sheathing failure since 1985 until 1995. The problem is caused by excessive exposure to solar radiation. Plywood is not safe because it contains glue that may be toxic, harmful to life and human skin when exposed to ignition. The aims of this research built on modifying plywood to be fire resistant. Thus, the sol - gel technique was applied to prepare a new fire-retardant coating containing different volumes of  $H_3PO_4$  (0, 0.3, 0.7, and 1.1 ml) to protect the plywood from ignition. The flammability properties of the different coated samples evaluated by the following measurements using standard methods: limiting oxygen index (LOI), ignitability and thermogravimetric analysis (TGA). The results indicated that, the highest flame retardant LOI obtained at  $H_3PO_4$  1.1ml reaching  $\approx 150\%$  relative to the un-treated; these results are supported through ignitability and thermogravimetric analysis.

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### Introduction

Wood is a polymeric material which made up of three major polymeric components, cellulose, hemicellulose and lignin [1-3]. It has many characteristics, as light weight, durability and excellent physical strength, and also it has been extensively studied because of its use as a construction material and as building materials, furniture, fuel, boats, bridges and shelter [4-8]. Charring materials as wood has complex interaction of mass transfer, chemistry and heat. When it is burning the char layer forms and increase from thermal analysis between sample outer layer and the pyrolysis front which responsible in decreasing the heat release rate after the first peak [9-15]. It is easy to ignite and flame spread [16]. The main role of fire-retardant materials is delaying the ignition and reducing the heat release rate of wood during the combustion [17]. The wood ignition can be classified into direct flame or in a glowing mode. The last method of wood ignition may or may not be followed by flaming at temperature around  $250^\circ C$  when exposed to the minimum heat flux ( $4.3 \text{ kW m}^{-2}$ ) possible for ignition, and that it invariably ignites, at least initially, in a glowing mode under these conditions [18]. Wood treatment with various flame-retardants as phosphorus compounds, and pentaerythritol were studied. Phosphorus compounds are important additives to award fire-resistance to otherwise flammable materials as textile, polymer, wood and paper. It is a fire resistance return to the covalent bonds which formed between the material surface and the coating [19].

Plywood is a type of panel products which has ignition properties very similar to solid wood. It is made of a strange number of thin layers glued together under pressure. When the process of thermal degradation achieved in the presence/absence of a limited amounts of oxygen, it is named pyrolysis. During the plywood pyrolysis the heat transfers from a heat source which lead to increase in temperature inside the fuel. This initial pyrolysis leads to release volatiles and char formation. These volatiles will be flowing towards the ambient resulting in heat transfer between hot volatiles and cooler un-pyrolysis fuel.

Some of volatiles will be condensed in the cooler parts of the fuel to produce tar and auto-catalytic [20].

This paper was built on synthesis a new fire resistant coating for plywood with sol-gel technique in the presence of phosphoric acid. The untreated and treated samples were exposed to thermal analysis tests as a differential scanning calorimeter and thermogravimetric analysis. The ignition characteristics of exposed surfaces of essentially flat samples were studied by using ignition tests as limiting oxygen index and ignitability instruments.

### Experimental

#### Materials & Chemical used

Plywood, methyltrimethoxysilane (95%) was purchased from Alfa Aesor, glacial acetic acid (99%), ethanol and phosphoric acid (85%) were purchased from Aldrich.

#### Sol-gel treatment

The sol-gel technique is used to prepare fire-retardant coating by mixing 5 ml methyltrimethoxysilane and 2.5 ml acetic acid as a catalyst under constantly stirring for 10 min at room temperature. A mixture of ethanol and distilled water was added (the silane film was dissolved in ethanol as soon as it is formed so that no layer or a mono layer is left on the surface, by this way, samples can be subjected to various surface sensitive techniques). The solution was stirred at ambient temperature for 60 min to complete hydrolysis and condensation reactions [21]. Finally, the phosphorylated sol-gel coatings were prepared as mentioned elsewhere [22].

#### Ignitability test

This test was carried out according to ISO 5657 (see Fig. 1) [23]. It can be defined as the easy way to study the combustion properties of different materials by exposing to heat flux. As we know that, the sample will be ignited when exposed to a high incident heat flux and slower if the incident heat flux is low. When the solid material ignites at the minimum temperature under specific test conditions this can be defined as ignition time [24].

Tele:

E-mail addresses: [dr\\_ahmedabdee@yahoo.com](mailto:dr_ahmedabdee@yahoo.com)

### Limiting oxygen index (LOI)

The LOI values were determined by using Rheometric scientific device according to ISO 4589-2 (see Fig. 2) [25] on the samples  $150 \times 50 \text{ mm}^2$ . The percentage in the  $\text{O}_2\text{-N}_2$  mixture deemed sufficient to sustain the flame was taken as the LOI value. Both nitrogen and oxygen were connected to the apparatus through pressure regulators. Determined  $\text{N}_2/\text{O}_2$  atmospheres were continuously sent through the glass chamber. After cutting the test sample in the previous dimension its clamped in the holder vertically in the center of the combustion column. The top of the sample was ignited using a propane gas burner. After 30 Sec from exposed the sample to the igniting flame we have two notes if the sample continued to burn after the flame source was removed or burning was stopped. If the ignition continues we have to change this sample with a new one and the oxygen concentration was controlled to a lower level, but if the sample ignition did not continue the oxygen concentration was increased to an intermediate value for the subsequent samples. Three or four replicates were tested for each sample to obtain the average LOI value [26].

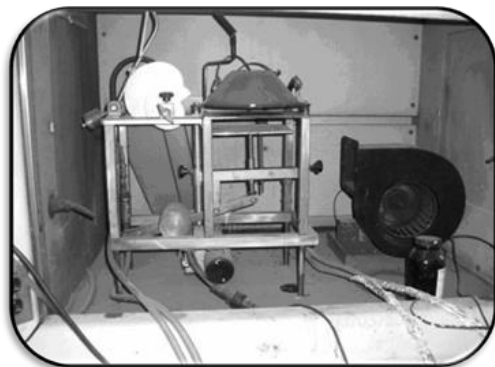


Figure 1: Ignitability instrument



Figure 2: LOI Instrument

### Thermogravimetric analysis (TGA)

TGA is the simplest technique, which used to determine the mass loss of a sample exposed to elevated temperatures [26, 27]. Simultaneous measurements of thermogravimetry (TG) of the untreated and treated samples were made in  $\text{N}_2$  on a DTG-50 thermal analyzer (Shimadzu). Put the sample in a crucible made of platinum then TGA measurements were carried out with a heating rate of  $10^\circ\text{C}/\text{min}$  up to  $750^\circ\text{C}$ .

### Differential Scanning Calorimetry (DSC)

It is used to measure heat flow (enthalpy,  $\Delta H$ ) and also glass transition ( $T_g$ ) through a sample of material compared to a standard/reference. This test was performed with DSC-50 Shimadzu Instrument - Japan. The heating rate was  $10^\circ\text{C}/\text{min}$  and the nitrogen gas was used as; a carrier gas and at a flow rate of 30 ml/min. Samples were repeated three times to

insure repeatability. Scans are started at temperature  $30^\circ\text{C}$  to a final temperature of  $650^\circ\text{C}$  [28, 29].

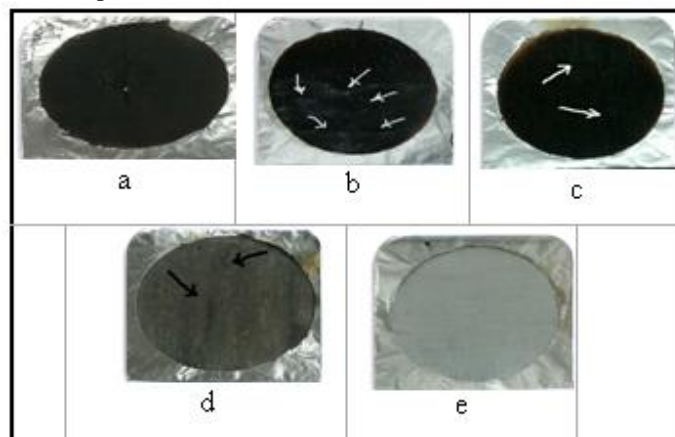


Figure 3: Different types of un-treated and treated plywood sample after ignition, a: un-treated sample after ignition, b: coated sample with sol-gel only, c: coated sample with sol-gel + 0.3 ml  $\text{H}_3\text{PO}_4$ , d: coated sample with sol-gel + 0.7 ml  $\text{H}_3\text{PO}_4$ , and e: coated sample with sol-gel + 1.1 ml  $\text{H}_3\text{PO}_4$

### Results

#### Ignitability

The capability of a material of being ignited can be defined as ignitability. It is properties for the samples were illustrated in Table 1. Figure 3 illustrates that, the untreated sample (a) was the highest char and more crack than other treated samples with sol-gel coating with different amount of phosphoric acid and completely destroyed after 9 min at heat flux  $10 \text{ kW}/\text{m}^2$  and 0.1 min at heat flux  $15 \text{ kW}/\text{m}^2$ . When the sample ignite under a limit heat flux in the presence of oxygen this lead to shrink the surface of wood sample (which made of made of different components affected with temperature) and hence loses its composition and residue as chars, this in case of blank one, but in case of treated sample (in the presence of different amount of  $\text{H}_3\text{PO}_4$ ) it is clear that, the protective layer of phosphorylated sol-gel playing an important role as sacrificial layer in protection of plywood from ignition. As we see here in Figure 3 that, sample (e) which coated with phosphorylated sol-gel including the highest percent of  $\text{H}_3\text{PO}_4$  recording the highest time to ignition when compared to the other samples.

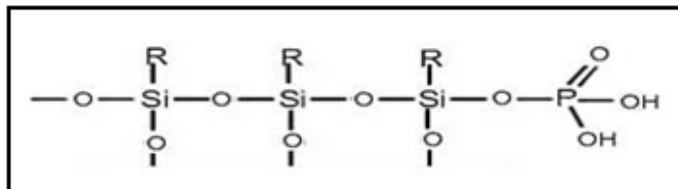
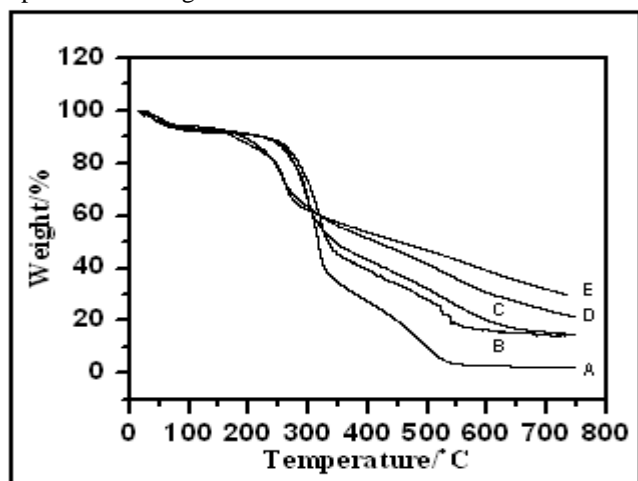


Figure 4: Mechanism of the reaction between siloxane and phosphoric acid [13]

#### LOI

This technique is used to measure the minimum percentage of oxygen in the test atmosphere that is required to slightly support combustion. Tables 1 illustrate the results of LOI on the untreated and treated samples under test. The untreated sample of plywood has ignited with LOI value 26.5 % combined with more smoke. The tabulated data refers to increase in the flame retardant properties of plywood from 26.5% (A) to 40% (E) by increasing the volume of  $\text{H}_3\text{PO}_4$  of sol-gel coating. This can be interpreted on mechanism as shown in Figure 4 [30]. Firstly, siloxane formed followed by reaction with  $\text{H}_3\text{PO}_4$  via hydrogen bond formation. Secondly, on increasing volumes of  $\text{H}_3\text{PO}_4$ , hydrogen bond formation increase, and spread on the surface of

the coated surfaces thus decreasing the oxygen reached to the sample surface so ignition decrease and LOI increase.



**Figure 5: TGA vs temperature for untreated and treated samples e in presence of  $N_2$  at rate  $10^\circ C/min$ . Since A: uncoated sample after ignition, B: treated sample by sol-gel technique in the absence of  $H_3PO_4$ , whereas, B, C, D and E revere to samples coated with phosphorylated sol-gel with different amounts of  $H_3PO_4$  0.3, 0.7 and 1.1 ml, respectively**

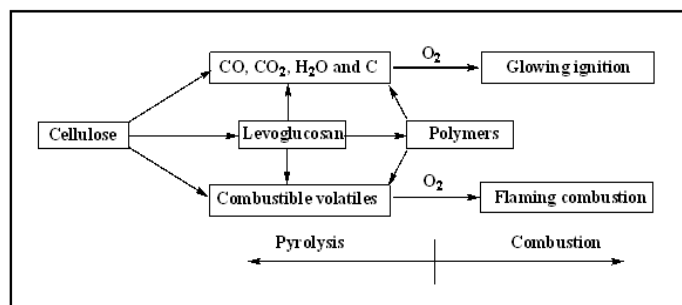
#### Thermal Analysis Results

From Figure 5 it can be found that the untreated sample was decomposed in three steps. At approximately  $131^\circ C$ , any moisture in the wood is vaporized out. Up to  $200^\circ C$  very little degradation occurred when chemical bonds start to break via dehydration. From  $200^\circ C$  whole wood starts to thermally degrade. The water vapor and CO from dehydration and decarboxylation processes that can reduce carbohydrate polymers are very slowly to a mostly carbon residue within these temperatures [31]. Between about  $300^\circ C$  and  $375^\circ C$ , the majority of the carbohydrate polymers have degraded into combustible volatiles and only lignin remains as being largely not degraded. The hemicellulose components start to decompose at about  $200^\circ C$  and are almost completely degraded by  $325^\circ C$ . The cellulose polymer is more stable to thermal degradation until about  $350^\circ C$  when it decomposes rapidly and almost completely over a very short temperature range. The decomposition of cellulose leads mainly to volatile gasses while lignin decomposition leads mainly to tars and char. In this research, the thermal stability and decomposition behaviors of the untreated and treated samples were estimated by TGA [32].

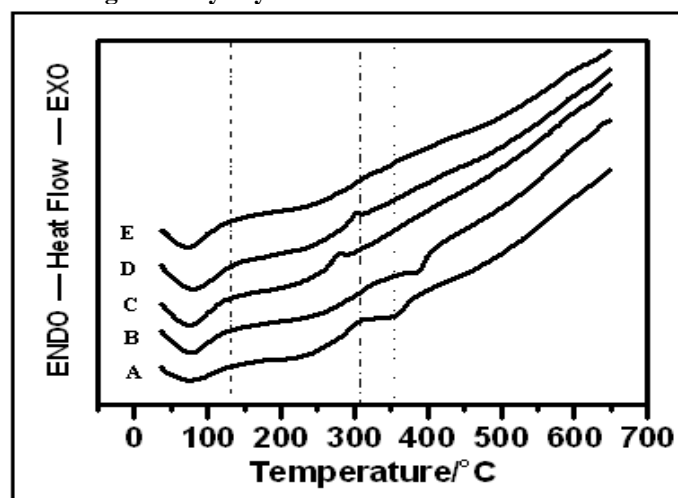
The pyrolysis steps and combustion of cellulose was shown in Figure 6. This Figure illustrates the pyrolysis and combustion of cellulose. In the early stages of cellulose degradation (below  $300^\circ C$ ), the molecular weight is reduced by depolymerization caused by dehydration reactions. The main products are CO,  $CO_2$  produced by decarboxylation and decarboxylation, water, and char residues. In the presence of oxygen, the char residues undergo glowing ignition. The formation of CO and  $CO_2$  are much faster in oxygen than in nitrogen and this rate accelerates as the temperature increases.

$T_{max}$  is the peak temperature which refers to the maximum rate decomposition temperature. In case of untreated sample, the beginning of the derivatives process occurred at temperatures ( $T_i$ ) close to  $195^\circ C$ , while in case of treated samples (B, C, D and E) the  $T_i$  recording 200, 98, 102 and  $109^\circ C$ , respectively. In Table 2 the  $T_f$  and residual mass at the  $750^\circ C$  start to increase by increasing the temperature until recording the highest value in the case of sample D and then start to decrease, this may be return to cracking the hydrogen bonds at the intermediate layer

in case of sample E more than the D one. Finally, in case of treated samples, the temperature at which 50% degradation occurs ( $T_{50\%}$ ) was shifted to higher values in comparison with un-treated one.



**Figure 6: Pyrolysis and combustion of cellulose**



**Figure 7: Differential scanning calorimeter curves for uncoated (A) and coated samples (B-E) with phosphorylated sol-gel after drying at  $100^\circ C$  for 20 min. Since A: uncoated sample after ignition, B: treated sample by sol-gel technique in the absence of  $H_3PO_4$ , whereas, B, C, D and E revere to samples coated with phosphorylated sol-gel with different amounts of  $H_3PO_4$  0.3, 0.7 and 1.1 ml, respectively**

#### Differential Scanning Calorimeter

The DSC for uncoated (A) and coated (B-E) samples with phosphorylated sol-gel with different volumes of  $H_3PO_4$  were shown in Figure 7 and tabulated in Table 3. The  $T_g$  was recorded the highest value in case of uncoated ( $60.2^\circ C$ ) and decrease by increasing the volume of  $H_3PO_4$  since sample E has the lowest  $T_g$  value ( $41.7^\circ C$ ). This may be returned to start to decompose the coated layer in case of samples B-E but in case of the uncoated sample just evaporated at  $100^\circ C$ . Figure 7 shows the first stage of decomposition (exotherm area) which appearing in the range of  $130-163^\circ C$ . At the previous temperature range a big difference was noticed at the heat flow of decomposition (sample A: +4.4, B: +5.5, C: +8.2, D: +7.9 and E: +7.7 J/g) between uncoated and coated samples. This may be return to form of sacrificial layer of coating over the plywood surface with strong bonds so it high energy to be cracking. In case of the second stage of decomposition, the exotherm area was noticed in all samples at different temperature, which refer to chemical reaction occurred between the sample surface and the coating. As shown in Figure 7, exotherm area was appeared at different temperatures. In case of sample D (0.7ml  $H_3PO_4$ ) it has the sharpest and smallest exotherm area than C, A, B and E, respectively. Finally, the  $T_{d3}$  and endotherm area were observed for both A ( $353.5^\circ C$  and -11.8 J/g) and B ( $367.0^\circ C$  and -8.5 J/g) samples. This may be returned to the total combustion of lignin in case of uncoated sample.

**Table 1: Studying the effect of different volumes of inorganic additives ( $H_3PO_4$ ) by LOI and ignitability on plywood samples**

Sample code	LOI (%)	$\Delta$ LOI (%)	Ignitability Test		
			Heat Flux ( $kW/m^2$ )	Time to ignition (Sec.)	Notes
A	26.5	---	10	550	• More smoke • Cleft completely
			15	8	
B	28.7	2.2	15	120	• More smoke • Cleft completely
C	33.7	7.2	15	131	• Little smoke • Cleft completely
D	35.1	8.6	15	159	• Little smoke • Partially completely
E	40	13.5	15	170	• Little smoke • No completely

Where as A: untreated sample after ignition, B: coated sample without  $H_3PO_4$ , C, D and E refer to coated samples with different volumes of  $H_3PO_4$  (0.3, 0.7 and 1.1ml), respectively.

**Table 2: Variables of the thermal degradation process of the untreated and treated samples in synthetic atmosphere nitrogen with a flow rate 20 ml/min**

Sample code	A	B	C	D	E	
$T_i$ ( $^{\circ}C$ )	195	200	98	103	109	
$T_f$ ( $^{\circ}C$ )	539	593	598	659	651	
$T_{max}$ ( $^{\circ}C$ )	I	268	257	197	219	242
	II	443	487	480	544	481
$T_{50\%}$ ( $^{\circ}C$ )	316	335	415	465	345	
Residual mass at 750 $^{\circ}C$ (%)	2.5	14.9	21.4	29.8	14.9	

$T_i$  = Temperature of initial decomposition,  $T_f$  = Temperature of final decomposition,  $T_{max}$  = Temperature of maximum decomposition and  $T_{50\%}$  = the temperature at which 50% degradation occurs.

**Table 3: Values of transition temperature and heat of fusion for untreated and treated samples**

Samples Data	$T_g$ $^{\circ}C$	$T_{d1}$ $^{\circ}C$	$\Delta H_1$ $/J g^{-1}$	$T_{d2}$ $^{\circ}C$	$\Delta H_2$ $/J g^{-1}$	$T_{d3}$ $^{\circ}C$	$\Delta H_3$ $/J g^{-1}$
A	60.2	131.2	+4.4	307.1	+9.57	353.5	-11.78
B	50.8	133.9	+5.5	319.5	+1.75	367.0	-8.5
C	47.3	139.4	+8.2	266.3	+9.0	----	----
D	46.6	162.4	+7.9	283.9	+5.5	----	----
E	45.5	143.3	+7.7	316.7	+2.5	----	----

while  $T_g$ ; glass-transition temperature,  $\Delta H_1$ ; first heat decomposition,  $T_{d2}$ ; temperature of the second decomposition,  $\Delta H_2$ ; second heat flow of second decomposition,  $T_{d3}$ ; temperature of the third decomposition,  $\Delta H_3$ ; third heat flow of third decomposition, A; blank sample, B; coated sample with sol-gel coating, C; coated sample with phosphorylated sol-gel coating (0.3ml  $H_3PO_4$ ), D; coated sample with phosphorylated sol-gel coating (0.7ml  $H_3PO_4$ ) and E; coated sample with phosphorylated sol-gel coating (1.1ml  $H_3PO_4$ ).

## Conclusion

The reaction of phosphorylated sol-gel coating was proceeding with the two stages; forming of silanol during the hydrolysis at first step then condensation process occurred to form siloxane. The basic of ignition and pyrolysis behaviors for plywood sample was tested by limiting oxygen index, ignitability, thermogravimetric analysis and differential scanning calorimetry. The cellulose up to 100 $^{\circ}C$  not affected by temperature but exposed to evaporate then starts to decompose at different stages. Starting from 300 $^{\circ}C$  up to 750 $^{\circ}C$  there was a decomposition stage for lignin. From fire tests we conclusion that there is a positive relationship between the limiting oxygen index and the volume of  $H_3PO_4$  as volume increase the LOI % increase. This data was proved by ignitability test. The previous results have been ratified by using ignitability, TGA and DSC tests.

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