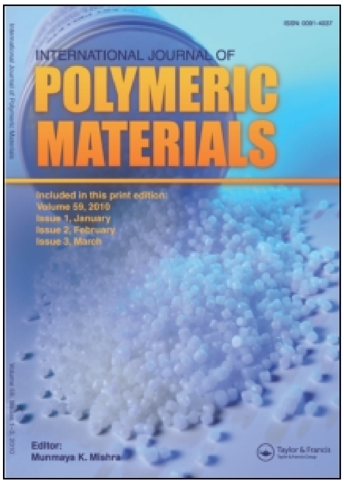

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Novel Low Flammable Coating Based on Polyvinyl Alcohol

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A new type of polymer varnish (coating) based on Polyvinyl Alcohol was developed using potassium permanganate oxidation in water solution. The flammability of this coating was tested using Cone Calorimeter. All tests on flammability indicated an increase of flame retardancy of this polymer coating due to carbonization of cross-linked polymer fragments.

Keywords: Coatings; water solution; polyvinyl alcohol; Flame retardancy; oxidation; char formulation

INTRODUCTION

Coatings based on water solution of polymers have large ecological advantage in comparison with nonaqueous polymer coatings. It is known [1] that irreversible coatings can be obtained from water solutions of PVA. The ammonium dichromate and UV-irradiation are used to oxidize PVA. The final product (coating) has a cross-linked structure and is insoluble in water or some other solvents.

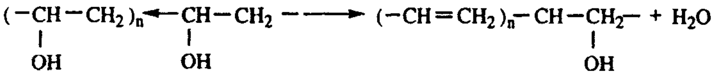
In the present work is described a way to get the similar results by using only potassium permanganate oxidation of PVA.

The second goal of this study was to evaluate the flammability of final coating which represents another ecological concern of polymer industry.

Flame retardants based on halogens (Cl, Br), heavy and transition metals (Zn, V, Pb, Sb) or phosphorus-organic compounds may reduce risk during polymer combustion and pyrolysis. They may, however, present ecological problems. While the overall use of halogenated flame retardants is still showing an upward trend, their ecological problems prompted intense search for environmentally friendly polymer additives.

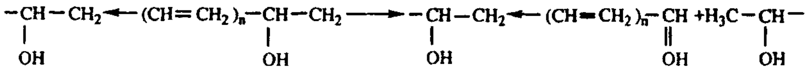
Our research focused on an ecologically-safe flame retardant system based on a high temperature polymer-organic char former, Polyvinyl alcohol. PVA acts by forming a char barrier which hinders the supply of oxygen and reduces the thermal conductivity of the material.

There is a strong correlation between char yield and fire resistance. This is because the char is formed at the expense of combustible gases and because the presence of a char inhibits further flame spread by acting as a thermal barrier around the unburned material. The tendency of a polymer to char can be increased with chemical additives and by altering its molecular structure. We have studied polymeric additives for polyvinyl alcohol systems which promote the formation of char. This polymeric additives usually produce a highly conjugated system – aromatic structures which char during thermal degradation and/or transform into cross-linking agents at high temperatures. Decomposition of PVA proceeds in two stages. The first stage, which begins at 200°C, mainly involves dehydration accompanied by formation of volatile products. The residues are predominantly polymers with conjugated unsaturated structures. In the second stage, polyene residues are further degraded at 450°C to yield carbon and hydrocarbons. The mechanism involved in thermal decomposition PVA has been deduced by Tsuchya and Sumi [2]. At 245°C water is split off the polymer chain, resulting in a residue with conjugated polyene structure:



$$(-\underset{OH}{CH}-CH_2)_n\leftarrow\underset{OH}{CH}-CH_2 \longrightarrow (-CH=CH_2)_n-\underset{OH}{CH}-CH_2- + H_2O$$

The scission of several carbon-carbon bonds leads to the formation of carbonyl ends. For example, aldehyde ends arise from the reaction:



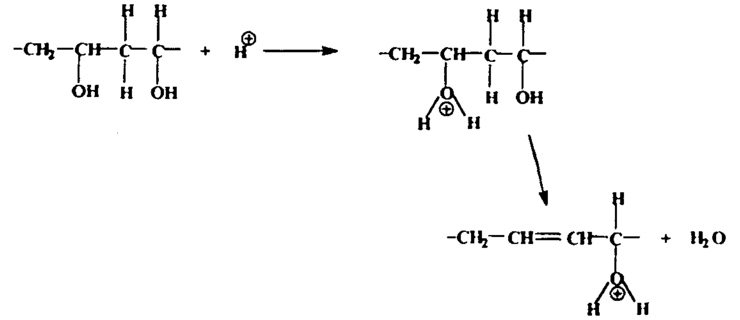
$$-\underset{OH}{CH}-CH_2\leftarrow(CH=CH_2)_n-\underset{OH}{CH}-CH_2 \longrightarrow -\underset{OH}{CH}-CH_2\leftarrow(CH=CH_2)_n-\underset{\substack{\| \\ OH}}{CH} + H_3C-\underset{OH}{CH}-$$

In the second-stage pyrolysis of PVA, the volatile products consist mainly of hydrocarbons, i.e. *n*-alkanes, *n*-alkenes and aromatic hydrocarbons [2].

Thermal degradation of PVA in the presence of oxygen can be adequately described by a two-stage decomposition scheme, with one modification. Oxidation of the unsaturated polymeric residue from dehydration reaction introduces ketone groups into the polymer chain. These groups then promote the dehydration of neighboring vinyl alcohol units producing a conjugated unsaturated ketone structure [3]. The first-stage degradation products of PVA pyrolysed in air are fairly similar to those obtained in vacuum pyrolysis. In the range 260°-280°C, the second-order-reaction expression satisfactorily accounts for the degradation of 80% hydrolyzed PVA up to a total weight loss of 40%. The activation energy of decomposition appears to be consistent with the value of 53.6 kcal/mol which is obtained from the thermal degradation of PVA [3].

The changes in the IR spectra of PVA subjected to heat treatment have been reported [3]. After heating at 180°C in air bands appeared at 1630 cm^{-1} (C=C stretching in isolated double bonds), 1650 cm^{-1} (C=C stretching in conjugated diens and triens), and 1590 cm^{-1} (C=C stretching in polyenes). The intensity of carbonyl stretching frequency at 1750-1720 cm^{-1} increased, although the rate of an increase of intensity was less than that of the polyene band at low temperatures. Above 180°C, although dehydration was the predominant reaction at first, the rate of oxidation increased after an initial induction period.

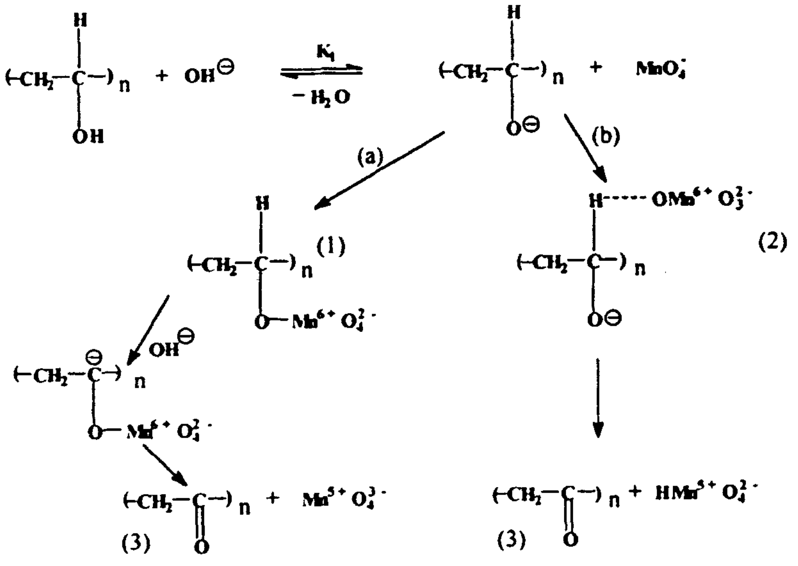
The identification of a low concentration of benzene among the volatile products of PVA has been taken to indicate the onset of a cross linking reaction proceeding by a Diels-Alder addition mechanism [4]. Clearly benzenoid structures are ultimately formed in the solid residue, and the IR spectrum of the residue also indicated the development of aromatic structures.



Acid-catalyzed dehydration promotes the formation of conjugated sequences of double bonds and Diels-Alder addition of conjugated and isolated double bonds in different chains may result in intermolecular cross linking producing structures which form graphite or carbonization products.

The next step in our plan to improve the flame resistant properties of poly(vinyl alcohol) – system was the substitution of a pure poly(vinyl alcohol) by poly(vinyl alcohol) oxidized by potassium permanganate (PVA-ox). This approach was based on the fire behavior of the (PVA-ox) itself. A dramatic decrease of the rate of the heat release and significant increase in ignition time has been noted for the oxidized PVA in comparison with the original PVA.

The literature on the oxidation of macromolecules by alkaline permanganate presents little information about these redox-systems. One set of workers [5, 6] investigated the oxidation of PVA as a polymer containing secondary alcoholic groups by **$KMnO_4$** in alkaline solution. It was reported that the oxidation of PVA in alkaline solutions occurs through formation of two intermediate complexes (1) and/or (2) [6]:



The reactions (a) and (b) lead to the formation of a poly(vinyl ketone) (3) as a final product of oxidation of the substrate. The poly(vinyl ketone) was isolated and identified by microanalysis and spectral data [7].

2. EXPERIMENTAL

Materials. The polymers used in this work was a poly(vinyl alcohol), 99 %, hydrolyzed, M. W. 86,000, (Scientific Polymer Products, Inc). The inorganic additive was potassium permanganate, R. (BA Chemicals Ltd.).

Preparation of samples, incorporation of additive. The samples for combustion measurements (PVA and PVA-ox) were compression molded at temperature 180–200°C for 10 min.

A poly(vinyl alcohol) was oxidized by $\mathbf{KMnO_4}$ in aqueous solution. A 10 % wt. aqueous solution of a poly(vinyl alcohol) was prepared at 90°C in a laboratory vessel (21). $\mathbf{KMnO_4}$ (5 % by wt. of original PVA) was added into the hot aqueous solution of PVA. After a fast reaction (1.5–2 min) the solution became dark-brown in color. It was allowed to cool to room temperature. Then water was removed under vacuum at 50°C to yield of soft elastic material. This material was heated in an oven for 24 hours at 120°C to give a hard plastic material. The resulting material was milled in a laboratory ball-mill to produce a dark brown powder.

Cone Calorimeter tests on the polymer samples, as discs (radius 35 mm), were carried out at 20, 30, 35 and 50 kW/m^2. Each specimen was wrapped in aluminum foil and only the upper face was exposed to the radiant heater.

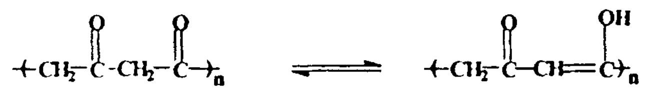
3. RESULTS AND DISCUSSION

Preliminary Cone tests for PVA and PVA oxidized by $\mathbf{KMnO_4}$ were carried out at heat fluxes of 20, 35 and 50 kW/m^2 (Tab. I). The yield of carbon residue (wt. %) and peak of heat release rate (Peak R. H. R. kW/m^2) suggest substantial improvement of fire resistance characteristics for PVA oxidized by $\mathbf{KMnO_4}$ in comparison with PVA. PVA oxidized by $\mathbf{KMnO_4}$ gives about half the peak of heat release rate (Peak R. H. R. kW/m^2), when compared with pure PVA. Even at

TABLE I Cone Calorimeter Data of PVA compositions

Material, Heat flux, kW/m²	*Initial wt., g*	*Char yield, % wt.*	*Ignition time, sec.*	*Peak R.H.R., kW/m²*	*Total Heat Release, MJ/m²*
PVA, 20	27.6	8.8	39	255.5	159.6
PVA, 35	28.3	3.9	52	540.3	111.3
PVA, 50	29.2	2.4	41	777.9	115.7
PVA-ox $KMnO_4$, 20	27.9	30.8	1127	127.6	36.9
PVA-ox $KMnO_4$, 35	30.5	12.7	774	194.0	103.4
PVA-ox $KMnO_4$, 50	29.6	9.1	18	305.3	119.8

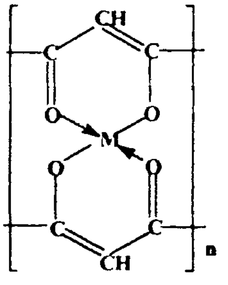
50 kW/m², the yield of char residue for PVA oxidized by $\mathbf{KMnO_4}$ was 9.1%. One reason for this phenomenon may be explained by the ability for PVA oxidized by $\mathbf{KMnO_4}$ – (polyvinyl ketone structures) to act as a neutral (structure 1) and/or monobasic (structure 2) bidentate ligand [7].



$$\left[CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}\right]_n \rightleftharpoons \left[CH_2-\overset{O}{\overset{\|}{C}}-CH=\overset{OH}{\overset{|}{C}}\right]_n$$

1 2

The experimental results of others (IR and electronic spectra) [9] provide strong evidence of coordination of the ligand (some metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}) through the monobasic bidentate mode (structure 2). Based on the above the following structure can be proposed for the polymeric complexes:



M - metal

The result of elemental analysis of PVA oxidized by **$KMnO_4$** indicates the presence of 1.5 % of **Mn** remaining in this polymeric structure. Thus, we suggest that this catalytical amount of chelated **Mn**-structure incorporated in the polymer may provide the rapid high-temperature process of carbonization and formation of char. The fire tests at 50 kW/m^2 for PVA compositions (a typical rate of heat release curves for each sample is shown in Fig. 1).

Similar trends are observed for Average Heat Release which was calculated over the total flame out period (Tab. I). The sample with PVA oxidized by **$KMnO_4$** displayed even some better flame retardant properties due to the catalytical effect of Mn-chelate fragments on the formation of char (Tab. I). The superior Rates of Heat Release properties of PVA oxidized **$KMnO_4$** are clearly shown by comparison of the values of Maximum Rate and Average Rate of Heat Release given in Figure 2.

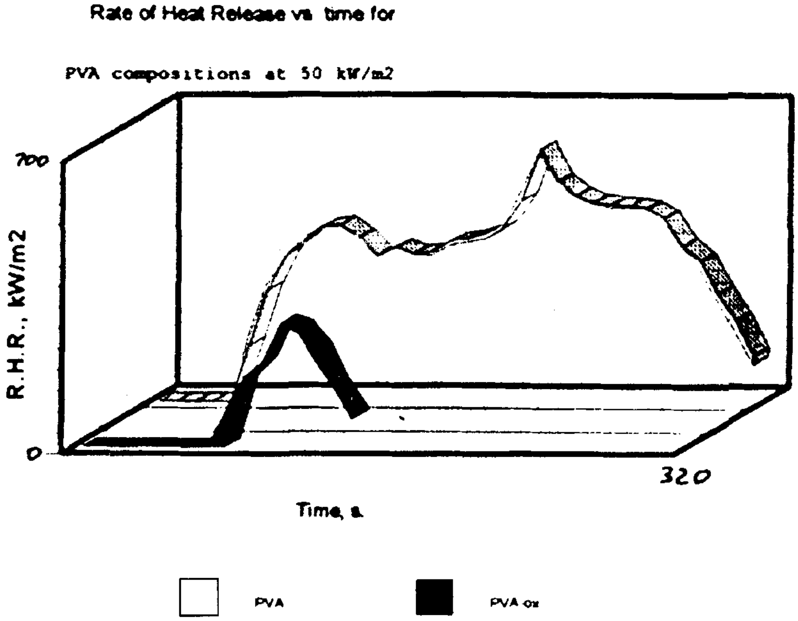


FIGURE 1

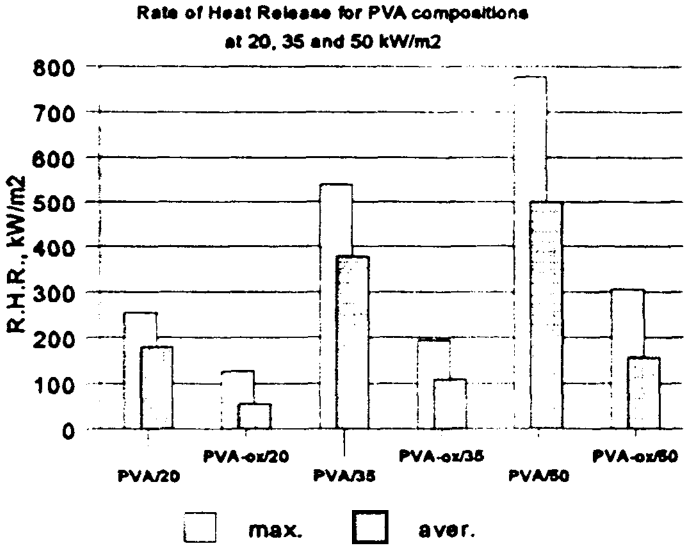


FIGURE 2

4. CONCLUSION

Polymeric char former such as PVA-ox may present a new type of ecologically-safe flame retardant system. It may be used as a cheap and safe polymer water insoluble coating (varnish).

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