

# ORGANOPHOSPHORUS AND ORGANO-INORGANIC HYBRID FIRE RETARDANT COATINGS FOR POLYMERS

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## Abstract

Thin coatings of crosslinked poly(vinylphosphonic acid) display good adhesion and excellent fire-retardant barrier properties when applied to the surfaces of a typical thermoplastic, such as poly(methyl methacrylate), but perform relatively poorly in water-soak tests. Water-soak test performance can be significantly improved however by various hydrophobic modifications without detriment to fire performance.

## Introduction

Coatings of crosslinked poly(vinyl phosphonic acid) (PVPA) prepared by room-temperature UV-initiated polymerization of mixtures of vinylphosphonic acid (VPA) and triallylcyanurate and using 2-hydroxy-2-methylpropiophenone as photoinitiator, have been shown to confer excellent fire retardance when applied to the surfaces of several textiles and glass fibre reinforced epoxy resin (GRE) composites [1, 2]. On textiles, polymerised vinyl phosphonic acid (VPA) produced self-extinguishing cotton, polyester and polyamide fabrics [1]. These coatings intumesce and char on exposure to flame, expanding by over 50 times their original thickness and, in doing so, offer substantial protection to the underlying polymer surface. In the work reported here, we have investigated the potential for similar coatings to fire protect more challenging thermoplastic materials, taking poly(methyl methacrylate) (PMMA) as a typical example.

## Experimental

PMMA sheets of 3 mm thicknesses were sourced from Lucite UK. Monomer, vinyl phosphonic acid (VPA), crosslinker triallyl isocyanurate (5 wt% w.r.t. VPA) and photo-initiator Darocur 1173 (5 wt% w.r.t. VPA) were used to make the coating. All the chemicals were mixed and stirred until a homogenous dispersion was achieved. The mixture was then applied on the PMMA surface to obtain coatings of ~0.3-0.4 mm thicknesses. Where inorganic additives (e.g., MgO) were used, coatings were prepared by triturating required amounts of inorganic chemicals in the coating mixture. The coatings were polymerised using UV irradiation, followed by post-curing at 80 °C for 24 h in an oven.

## Results and Discussion

Table 1 gives typical cone calorimetric data for an uncoated PMMA plaque (75 mm x 75 mm x 3 mm) and one coated with crosslinked PVPA (10 wt% triallyl cyanurate). Note that a 0.4 mm PVPA coating intumesces by a remarkable 7600% when exposed to radiant heating at 35 kW/m<sup>2</sup> and prevents ignition of the underlying PMMA completely, so acting as a fire barrier in the same manner as it does with GRE.

**Table 1.** Typical cone calorimetric data for PVPA-coated and uncoated PMMA plaques at a radiant heat flux of 35 kW/m<sup>2</sup> with no source of ignition

Sample	Coating thickness (mm)	Char height (mm)	TTI (s)	TTFO (s)	PHRR (kW/m <sup>2</sup> )	TTPH (s)	THR (MJ/m <sup>2</sup> )
PMMA	N/A	N/A	89	275	900	150	79
PMMA/PVPA	0.42	32.0	No ignition				

TTI = time to ignition, TTFO = time to flame out, PHRR = peak heat release rate, TTPH = time to peak heat release rate, THR = total heat released

PVPA coatings also show good adhesion to PMMA with as little as 0.04% mass of coating removed in a tape-pull test, but poor performance in water soak tests, with up to 90% of coating removed after soaking in water at RT for 24 h. This poor water-soak performance is undoubtedly due to the inherent hydrophilicity of PVPA.

In attempts to improve the hydrophobicity, and thus the water-soak performance, of PVPA coatings, we have investigated using a range of inorganic fire retardant additives in the coatings. Here the effects on coating performance of adding small amounts of MgO to VPA has been discussed. Tape-pull and water-soak test results and cone calorimetric data for PVPA/MgO coating formulations when applied to a PMMA substrate are given in Tables 2 and 3, respectively.

**Table 2** Tape-pull and water-soak test results for PVPA/comonomer coatings on PMMA

Coating	Thickness (mm)	Tape-pull test (wt% removed)	Water-soak test (wt% removed)
PVPA	0.42	0.04	89
PVPA/MgO (1 wt%)	0.25	0.19	54
PVPA/MgO (5 wt%)	0.36	0.34	52
PVPA/MgO (10 wt%)	0.55	0.09	40

**Table 3.** Cone calorimetric data for variously coated PMMA plaques at a radiant heat flux of 35 kW/m<sup>2</sup>

Coating	Coating thickness (mm)	Char height (mm)	TTI (s)	TTFO (s)	PHRR (kW/m <sup>2</sup> )	TTPH (s)	THR (MJ/m <sup>2</sup> )
PVPA	0.42	32	No ignition				
PVPA/MgO (1%)*	0.37	27	No ignition				
PVPA/MgO (1%)*	0.44	36	723	1028	257	765	38
PVPA/MgO (5%)	0.53	34	378	659	343	425	62
PVPA/MgO (10%)	0.67	34	519	775	449	525	39

\* Replicate experiments indicating non-reproducibility of behaviour with this formulation

From Table 2 it can be seen that addition of MgO to PVPA significantly improves the performance in the water-soak test with best results achieved at the highest MgO concentration, as might be expected. However, even at 10 wt% MgO, 40% of the coating is removed by water soaking. In cone calorimetric experiments, a coating of PVPA containing 1% MgO was found, like PVPA itself, to be capable of preventing ignition of a PMMA plaque, although as can be seen from the two sets of data for such coatings given in Table 3, this effect was not reproducible. With coatings containing higher loadings of MgO, ignition of PMMA was invariably observed, although this was significantly delayed compared with ignition in uncoated PMMA, and peak heat release rates and total heats released were significantly reduced. The main problem encountered with PVPA/MgO coatings was that viscosities prior to polymerisation were high, making even coating of PMMA plaques difficult. It is possible that the poorer fire performance of the coatings containing most MgO arise from inhomogeneities in the coatings leading to microregions where the coatings are thinner than the measured average thickness, thus offering less protection. These and other aspects of our work will be discussed more fully at the conference.

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### References

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