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Polymer 40 (1999) 4093–4098

polymer

An oxygen index evaluation of flammability on modified epoxy/polyester systems

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Received 22 April 1998; accepted 18 August 1998

Abstract

This article describes a study on flame retardancy conducted on a dual cure thermosetting system consisting of an epoxy resin, blended with an unsaturated polyester. Neat resin panels and glass-fibre reinforced composites were prepared utilising several structurally different flame-retardant (FR) additives. These materials were tested in order to determine the Limiting Oxygen Index (LOI), which is a measure of the fire performance properties of a given material. Particular attention was paid to the FR properties of compounds, which are free of halogen such as bromine, in the absence of antimony oxide. These compounds are based on phosphorous containing molecules.

Keywords: Flame retardant; Intumescent; LOI

1. Introduction

Flame retardation is a process by which the normal degradation or combustion processes of polymers is altered by the addition of certain chemicals. Some plastic materials are inherently, to a relative degree, fire retardant or smoke retardant and their fire performance is acceptable for certain applications. However, for many plastic materials, it is necessary to improve their fire performance by incorporating commercially available flame retardants. Retardants are expected to be effective in improving fire performance without excessive loss of other important performance characteristics.

Concerns about the environment have increased in recent years and those concerns affect plastics and flammability in various ways. Concern about the atmospheric ozone layer results in reduction in the use of clorofluorocarbons and their replacement with alternate materials. However, clorofluorocarbons contribute to fire resistance and the alternate materials may contribute less to fire resistance.

A wide range of flame retarding additives were used to improve the fire resistance of an epoxy/polyester system. Well-known inorganic flame retardants (bromine/aluminium oxide trihydrate/antimony trioxide/red phosphorus) were used to determine the baseline properties of the resin.

Further, the effect of different kinds of phosphorus containing organic monomers were analysed. The aim was to establish the effect of unreactive and reactive P-additives (Fig. 1a and b) on the flame behaviour of the epoxy/polyester system and to make a comparison with the inorganic flame retarded formulation. At present halogenated compounds used in synergism with antimony are considered to be the most efficient flame retardants, but current research is looking towards environmentally friendly additives in the form of organo–phosphorus compounds [1–3].

2. Experimental

The basic system consists of an epoxy resin, diglycidylether of bisphenol A, (DER 330, Dow Chemical) cured by methyl-5-norbornene-2, 3-dicarboxylic anhydride (Ac-Methyl, LONZA) together with the catalyst 2-ethyl-4-methyl imidazole (EMI-24, ARTEL) and an unsaturated polyester which is pre-thickened. The system is then thermally postcured in order to complete the epoxy/anhydride reaction [4].

2.1. Preparation of neat resin panels

The resin was placed in a 6 × 4 in. mould, pre-thickened and stored for a period of 16 h in an oven heated at 80°C.

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0032-3861/99/$ - see front matter
PII: S0032-3861(98)00646-6

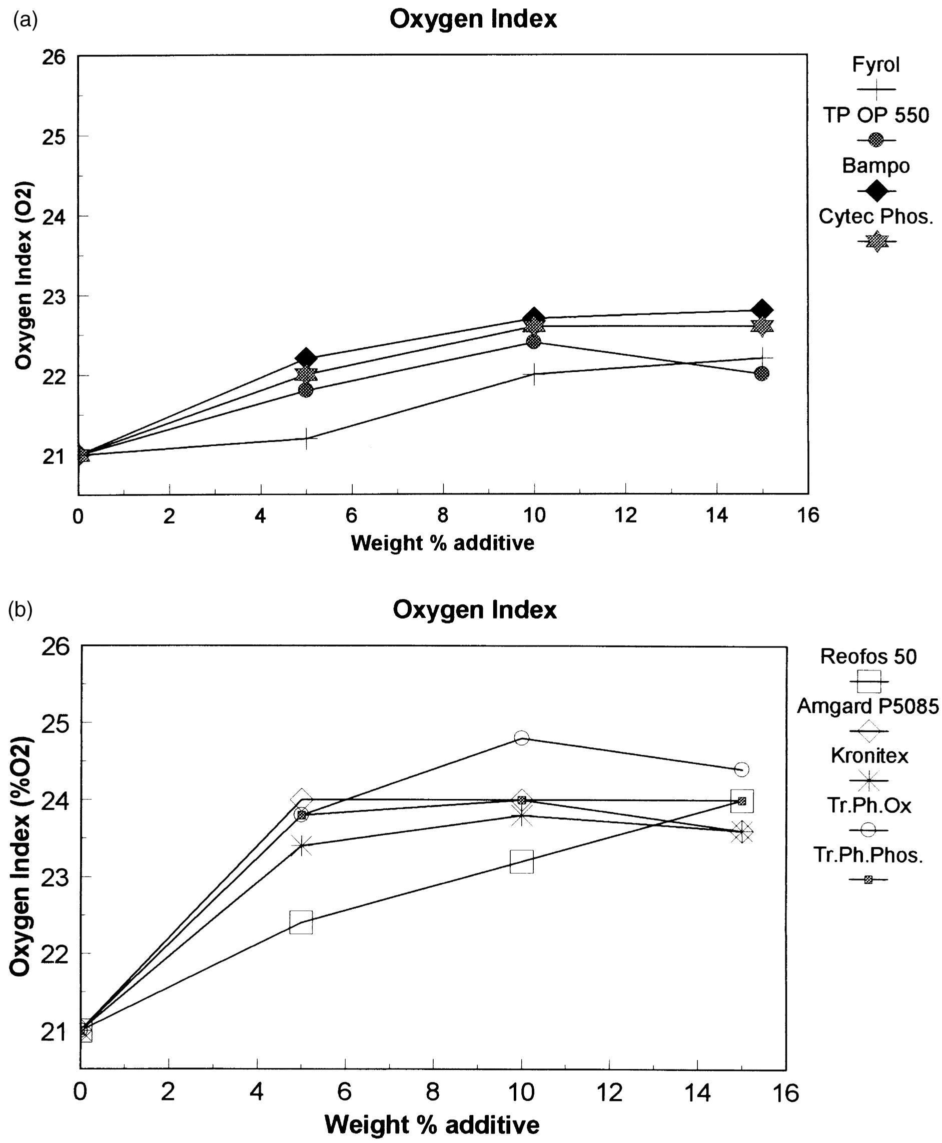


Fig. 1. (a) LOI vs. weight % of reactive P-additives in the epoxy resin (b) LOI vs. weight % of unreactive P-additives.

2.2. Preparation of glass fibre prepeg

The material supplied by Fiberite was used, which was an uni-directional glass product held together by stitching.

Individual sheets of glass fibre were pre-cut in dimensions of about 6×4 in^2. For each laminate six sheets were used. The individual glass fibre sheets were placed inside polythene bags. The resin was then injected from a syringe onto the surface of the glass. The amount of resin required was calculated to give a 40% resin solids content.

The individual sheets were assembled into six ply laminates.

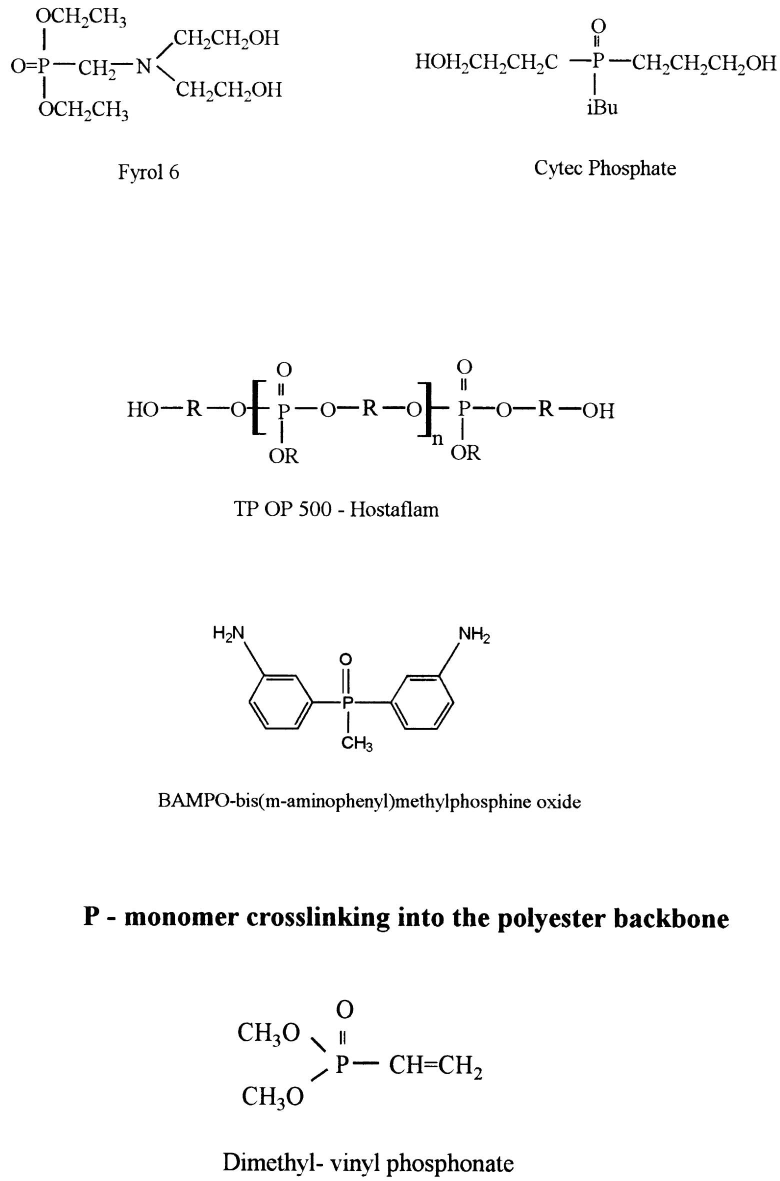
2.3. Flame retardant formulations

A brominated polyester Hetron FR 1540 was used in synergism with antimony trioxide (Sb2O3), aluminiumoxide trihydrate (ATH) and red phosphorus (Masteret 70450). Several combinations were tested to determine the effect of each additive in the epoxy/polyester formulation.

Halogen-free flame retarded formulations were prepared by adding to the standard resin different amounts (5%, 10%, 15%) of unreactive and reactive P-monomers (Schemes 1 and 2).

2.4. Limit Oxygen Index determination

Limiting Oxygen Index (LOI) is the minimum concentration of oxygen, determined in a flowing mixture of oxygen and nitrogen that will just support flaming combustion of the material [5–8]. The oxygen concentration of the mixture used in each successive test is increased or reduced by a small amount until the required concentration is reached. All the tests were carried out according to the British



Scheme 1.

Standard Method (BS 2782), PartC, which describes the procedure for testing plastic samples cut from rigid sheet.

The instrument used was a Stanton Redcroft provided with an Oxygen Analyser. Five strips were cut from each sample by a diamond saw. The required dimensions were: width (10 mm), length (50 mm), thickness (1.2–6.5 mm). Each specimen was clamped vertically in the centre of the column and was allowed to burn for a length of 50 mm or for the period of 3 min.

3. Results and discussions

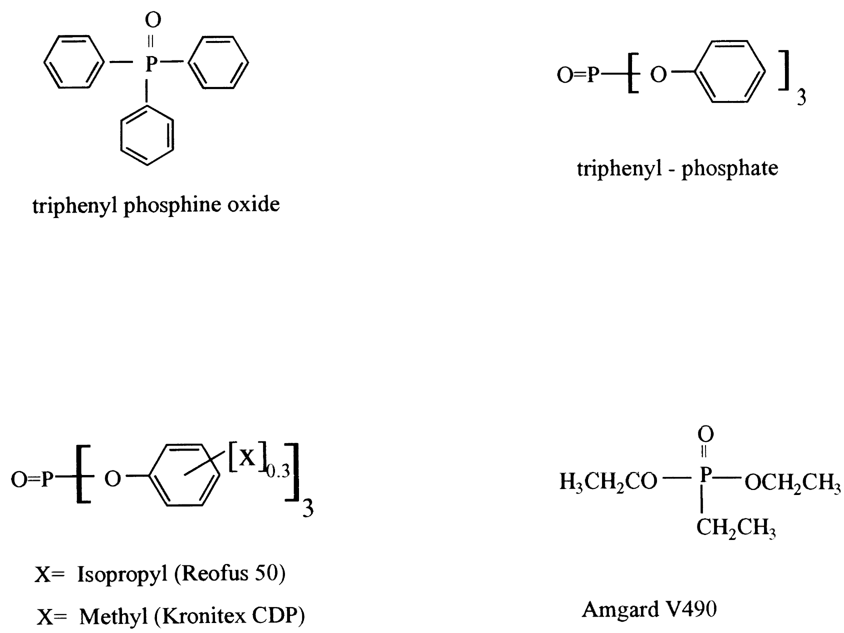
The LOI value of the standard epoxy/polyester formulation lies in the typical range of epoxy and polyester resins (Table 1). The presence of glass fibre in the composite panel increases the LOI value since the glass acts as a physical barrier against the flame. The full retarded formulation (II) shows the highest LOI value resulting from the synergistic work of all the additives:

Antimony trioxide act as a synergist with halogens, particularly with bromine (IX), while it is almost totally ineffective when used without halogen (IV). Synergism occurs through a series of reactions; the basic reaction in the case of brominated flame retardants is:

$$Sb_2O_3 + 6HBr \Leftrightarrow 2SbBr_3 + 3H_2O$$

Antimony tribromide forms a dense white smoke that snuffs the flame by excluding oxygen from the front of the flame.

Aluminium oxide trihydrate decompose to produce water



Scheme 2.

Table 1
LOI values of inorganic FR

Sample	FR additives	Loading (%)	LOI neat resins	LOI GF/resins
I	Standard	11.2	*21*	*27.8*
II	Hetron (Br)	13.2		
II	Masteret (P)	15.4	*26.4*	*41.4*
II	ATH	25.3		
II	Sb_2O_3	2.2		
III	Hetron (BR)	19.5	23.4	32
IV	Sb_2O_3	3.2	20.4	
V	ATH	25.3	21.8	
VI	ATH	40	21.8	
VII	Masteret	15.4	22	
VIII	Kronitex	5	23.4	31.4
IX	Hetron	18.9	*27.6*	*38*
IX	Sb2O3	3.2		
X	Hetron	14		33.2
X	ATH	25		
XI	Hetron	12.9		
XI	ATH	23	24.6	
XI	Sb2O3	2.17		
XII	Hetron	16	25	34
XII	Masteret	18.66		
XIII	Hetron	12.2		
XIII	Masteret	14.3	27.2	40.8
XIII	ATH	23.4		
XIV	Masteret	14	25	38.4
XIV	ATH	25		
XV	Hetron	18.4	23.6	32.4
XV	Kronitex	4.76		
XVI	Hetron	12		
XVI	Kronitex	5	23.6	33.6
XVI	ATH	25		

vapour. Heat is absorbed because of decomposition as well as vaporisation of liquid water. Further, $Al_2O_3, \cdot 3H_2O$ does not generate smoke and when used in combination with other flame retardants (FR), reduces the smoke production.

Red phosphorus in a mixture with 50% of epoxy resin (Masteret) was used. In the presence of heat and oxygen, phosphorus compounds decompose to form water vapour and phosphorus oxides, which react with hydrocarbon fragments to produce a very high melting point char at the interface between the polymer and the heat source. The chars rapidly dissipate heat energy and lose their glow. This anti-glow property of phosphorus contributes to its effectiveness as a flame retardant.

Synergism also occurs between phosphorus and

Table 2
LOI of unreactive P-additives

Additive	Loading (%)	LOI
–	–	21
Reofus	5	22.4
Reofus	10	23.2
Reofus	15	24
Kronitex	5	23.4
Kronitex	10	23.8
Kronitex	15	23.6
Amgard	5	24
Amgard	10	24
Amgard	15	23.6
Tr. Ph. Phos. Ox.	5	23.8
Tr. Ph. Phos. Ox.	10	24.8
Tr. Ph. Phos. Ox.	15	24.4
Tr. Ph. Phosphate	5	23.8
Tr. Ph. Phosphate	10	24
Tr. Ph. Phoshate	15	24

Table 3
LOI values of P-additives reacting in the epoxy phase

Additive	Loading (%)	LOI
Neat panels		
–	–	21
Fyrol 6	5	21.2
Fyrol 6	10	22
Fyrol 6	15	22.2
TP OP 550	5	21.8
TP OP 550	10	22.4
TP OP 550	15	22
Cytec Phosphate	5	22
Cytec Phosphate	10	22.6
Cytec Phosphate	15	22.6
BAMPO	5	22.8
BAMPO	10	23
BAMPO	15	23.2
Glass-fibre composite		
BAMPO	5	32.8
BAMPO	10	32.4
BAMPO	15	30.6

bromine (XII) and between phosphorus and ATH (XIV). Phosphorus–bromine synergism can be explained because phosphorus promotes the formation of char which further restricts movements in the gaseous phase, and results in the formation of phosphorus oxybromide and phosphorus tribromide which are less readily gasified.

3.1. Limiting Oxygen Index results of unreactive P-additive formulations

The presence of a small amount of unreactive phosphorus additives increases considerably the LOI value of the epoxy/polyester formulation, and in fact changes from 21 to 24 after adding only 5% of Amgard.(Table 2) The loading of additive does not affect the LOI value which is almost constant at different levels of P-monomer addition. The char yield during combustion looks expanded and foamed and this is a typical characteristic of intumescent chars. The presence of phosphorus in the formulation contribute to produce an unconventional intumescent cha, which improves the fire resistance and hence increases the LOI value.

3.2. Limiting Oxygen Index results of reactive-phospate formulations

Table 3 reports LOI values of samples containing phosphate monomers reacting in the epoxy phase. The aim is to obtain the P monomer to crosslink into the epoxy/anhydride phase and then establish its effect upon the cured materials flammability. According to the LOI figures, there is no significant variation between the different additives used (Fig. 2).

Further, the LOI values are not affected by the level of P-additive, in fact a loading of 5% of additive gives almost the same LOI than 15%. This is obviously a positive effect

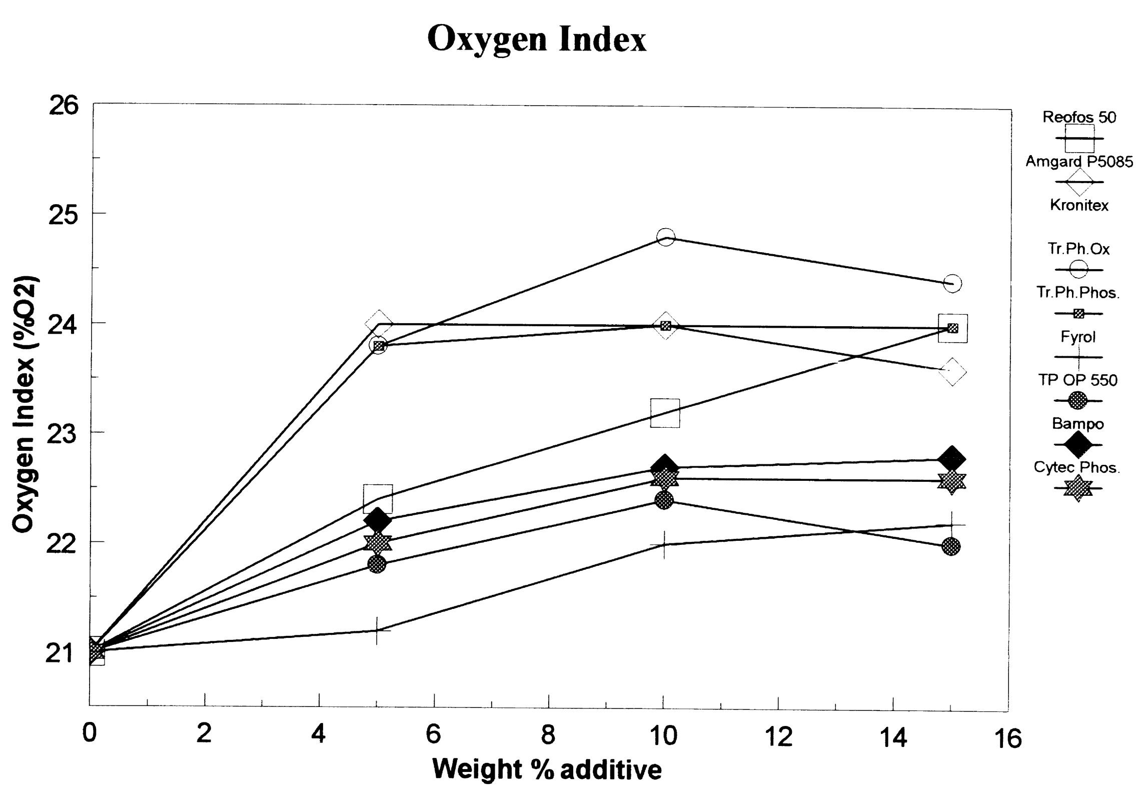


Fig. 2. Comparison of LOI figures of unreactive and reactive P-additives.

because a small amount of P-additive is enough to improve the flame resistance.

Only one monomer reacting in the polyester backbone has been tested. The samples were prepared by replacing all of the styrene with 5% of dimethyl–vinyl phosphonate $(CH_3O)2POCH = CH_2$. The LOI value of the neat panel was 21.2, while for the glass-fibre/composite it was 32.2 and both values are very similar to those of Table 3. The results of this work demonstrate the effectiveness of P based molecules on the flame retardancy of epoxy/anhydride cured.

The comparison between reactive and non reactive P based molecules suggests, according to the LOI figures, that either chemistry has a significant effect upon increasing the flame resistant properties of the resin. However, other tests are required to establish the effects of not only the P based molecules but also of the other additives such as alumina trihydrate and the halogenated polyester on aspects of flame retardancy.

4. Conclusions

The promotion of char formation [9] is perhaps the most important overall concept in fire-retarding plastic materials, as retention of carbon in the char has several beneficial effects, such as reduction of the heat of combustion, reduction of smoke evolution, reduction of oxygen depletion and reduction of toxic gas evolution, particularly carbon monoxide. The presence of small amounts of FR increases the LOI value of the epoxy/polyester formulation. The combination of P and antimony trihydrate (ATH) gives a good intumescent halogen-free system.

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