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Ecological Aspects of Polymer Flame Retardation

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Ecological Aspects of Flame Retardant Polymer Compositions are reviewed. Conclusions regarding their potential ecological problems are presented.

Keywords: Flame retardants; halogenated dioxins; toxicity polymeric char formers

INTRODUCTION

Plastics have played an important role in sharpening our history. After the invention of the celluloid billiard ball in 1860's, plastics demonstrated their endless possibilities. Since then, plastics have become an integral part of our everyday life.

The interest in flame retarding plastics goes back to the mid nineteenth century with the discovery of highly flammable cellulose nitrate and celluloid. In more recent times the conventional large volume of plastics such as phenolics, rigid PVC and melamine resins possess adequate flame retardancy. By the 1970's the major flame retardant polymers were the thermosets, namely, unsaturated polyesters and epoxy resins which utilized reactive halogen compounds and alumina hydrate as an additive. There was also a large market for phosphate esters in plasticized PVC, cellulose acetate film, unsaturated polyesters

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and modified polyphenylene oxide. Alumina trihydrate (ATH) was the largest volume flame retardant into unsaturated plastics. Consumption of halogen-containing flame retardant additives in 70's was much less than the other additives. The halogenated flame retardant additives were Dechlorane Plus, a chlorinated ahylic (for polyolefins), tris-(dibromopropyl) phosphate, brominated aromatics, pentabromochloro-cyclohexane and hexabromocyclododecane (for polystyrene). The next five years was to see a number of new brominated additives on the market. There were produced a number of chlorinated flame retardant products under the Dechlorane trade name. The products included of two moles of hexachlorocyclopentadiene and contained 78% chlorine, Dechlorane Plus, a Diels-Alder reaction product of cyclooctaliene and hexachlorocyclopentadiene with 65% chlorine, a Diels-Alder product with furan and a product containing both bromine and chlome with 77% halogen developed for the polystyrene and ABS materials.

In 1985–86 a German study detected brominated dioxins and furans from pyrolysis of a brominated diphenyl oxide in the laboratory at 510–630°C. The relevance of these pyrolysis studies to the real hazard presented by these flame retardants under actual use conditions has been questioned. Germany and Holland have considered a ban or curtailed use of brominated diphenyl oxide flame retardants because of the potential formation of highly toxic and potentially carcinogenic brominated furans and dioxins during combustion. The issue spread to other parts of Europe where regulations were proposed to restrict their use. Nevertheless, demand for brominated flame retardants including decabromo- and pentabromodiphenyl oxides continues to be strong and growing.

HALOGENATED DIPHENYL ETHERS, DIOXINS

Chlorinated dibenzo-*p*-dioxins and related compounds (commonly known simply as dioxins) are contaminants present in a variety of environmental media. This class of compounds has caused great concern in the general public as well as intense interest in the scientific community. Laboratory studies suggest the probability that exposure to dioxin-like compounds may be associated with other serious health

effects including cancer. Recent laboratory studies have provided new insights into the mechanisms involved in the impact of dioxins on various cells and tissues and, ultimately, on toxicity. Dioxins have been demonstrated to be potent modulators of cellular growth and differentiation, particularly in epithelial tissues. These data, together with the collective body of information from animal and human studies, when coupled with assumptions and inferences regarding extrapolation from experimental animals to humans and from high doses to low doses, allow a characterization of dioxin hazards.

Polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) are chemically classified as halogenated aromatic hydrocarbons. The chlorinated and brominated dibenzodioxins and dibenzofurans are tricyclic aromatic compounds with similar physical and chemical properties, and both classes are similar structurally. Certain of the PCBs (the so-called coplanar or mono-ortho coplanar congeners) are also structurally and conformationally similar. The most widely studied of these compounds is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). This compound, often called simply dioxin, represents the reference compound for this class of compounds. The structure of TCDD and several related compounds is shown in Figure 1.

These compounds are assigned individual toxicity equivalence factor (TEF) values as defined by international convention (U.S.EPA, 1989). Results of *in vitro* and *in vivo* laboratory studies contribute to the assignment of a relative toxicity value. TEFs are estimates of the toxicity of dioxin-like compounds relative to the toxicity of TCDD, which is assigned a TEF of 1.0. All chlorinated dibenzodioxins (CDDs) and chlorinated dibenzofurans (CDFs) with chlorines substituted in the 2, 3, 7, and 8 positions are assigned TEF values. Additionally, the analogous brominated dioxins and furans (BDDs and BDFs) and certain polychlorinated biphenyls have recently been identified as having dioxin-like toxicity and thus are also included in the definition of dioxin-like compounds. Generally accepted TEF values for chlorinated dibenzodioxins and dibenzofurans are shown in Table I.

A recent World Health Organization/International Program on Chemical Safety meeting held in The Netherlands in December 1993 considered the need to derive internationally acceptable interim TEFs

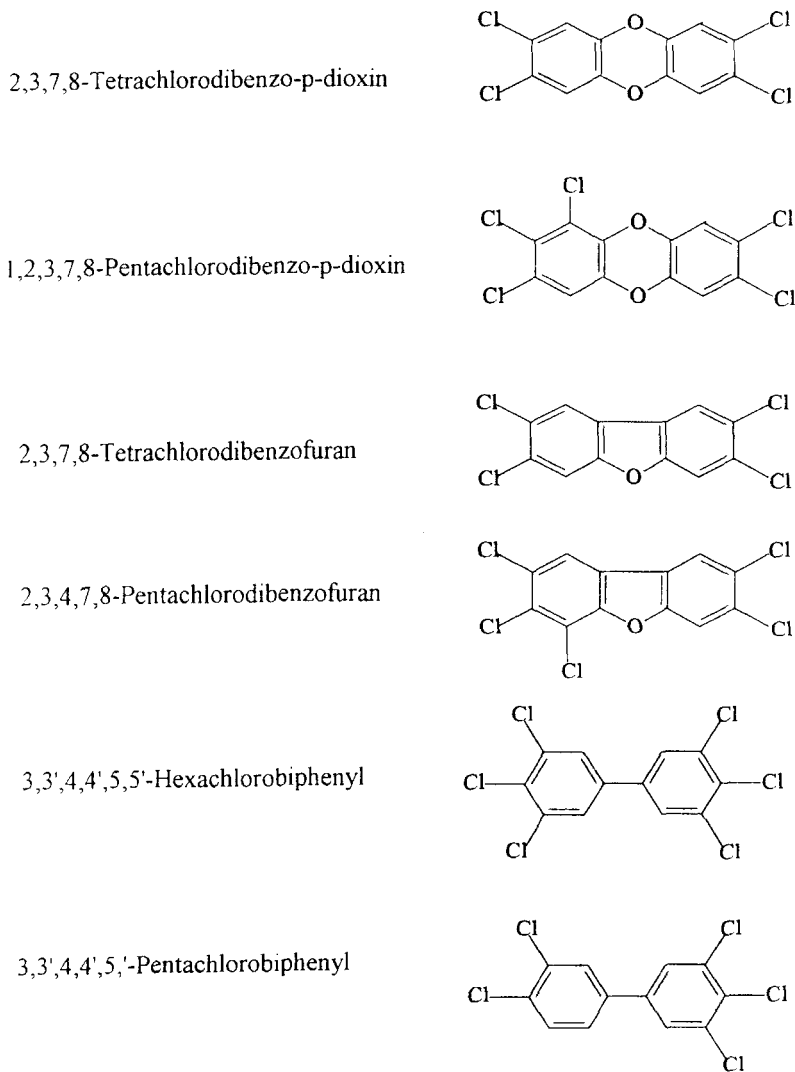


FIGURE 1 The structures of dioxin and similar compounds.

for the dioxin-like PCBs. Recommendations arising from that meeting of experts [1] suggest that in general only a few of the dioxin-like PCBs are likely to be significant contributors to general population exposures to dioxin-like compounds. Dioxin-like PCBs may be

TABLE I Toxicity Equivalency Factors (TEF) for CDDs and CDFs

<i>Compound</i>	<i>Toxicity Equivalency Factors, TEF</i>
Mono-, Di-, and Tri-CDDs	0
2,3,7,8-TCDD	1
Other TCDDs	0
2,3,7,8-PeCDD	0.5
Other PeCDDs	0
2,3,7,8-HxCDD	0.1
Other HxCDDs	0
2,3,7,8-HpCDD	0.01
Other HpCDDs	0
Mono-, Di-, and Tri-CDFs	0
2,3,7,8-TCDF	0.1
Other TCDFs	0
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
Other PeCDFs	0
2,3,7,8-HxCDF	0.1
Other HxCDFs	0
2,3,7,8-HpCDF	0.01
Other HpCDFs	0
OCDF	0.001

responsible for approximately one-fourth to one-half of the total toxicity equivalence associated with general population environmental exposures to this class of related compounds.

There are 75 individual compounds comprising the CDDs, depending on the positioning of the chlorine(s), and 135 different CDFs. These are called individual congeners. Likewise, there are 75 different positional congeners of BDDs and 135 different congeners of BDFs. Only 7 of the 75 congeners of CDDs or of BDDs are thought to have dioxin-like toxicity; these are ones with chlorine/bromine substitutions in, at least, the 2, 3, 7, and 8 positions. Only 10 of the 135 possible congeners of CDFs or of BDFs are thought to have dioxin-like toxicity; these also are ones with substitutions in the 2, 3, 7, and 8 positions. While this suggests 34 individual CDDs, CDFs, BDDs, or BDFs with dioxin-like toxicity, inclusion of the mixed chloro/bromo congeners substantially increases the number of possible congeners with dioxin-like activity. There are 209 PCB congeners. Only 13 of the 209 congeners are thought to have dioxin-like toxicity; these are PCBs with 4 or more chlorines with just 1 or no substitution in the ortho position. These compounds are sometimes referred to as coplanar, meaning that

they can assume a flat configuration with rings in the same plane. Similarly configured polybrominated biphenyls are likely to have similar properties; however, the data base on these compounds with regard to dioxin-like activity has been less extensively evaluated. Mixed chlorinated and brominated congeners also exist, increasing the number of compounds considered dioxin-like. The physical/chemical properties of each congener vary according to the degree and position of chlorine and/or bromine substitution. Very little is known about occurrence and toxicity of the mixed (chlorinated and brominated) dioxin, furan, and biphenyl congeners.

In general, these compounds have very low water solubility, high octanol-water partition coefficients, and low vapor pressure and tend to bioaccumulate.

Although these compounds are released from a variety of sources, the congener profiles of CDDs and CDFs found in sediments have been linked to combustion sources [3].

The Hazards Substance Ordinance in Germany specifies the maximum level of chlorinated dibenzodioxins and furans that can be present in materials marketed in Germany. This has been extended to the brominated compounds. The two largest volume flame retardants decabromodiphenyl oxide and tetrabromo bis-phenol A are said to meet these requirements [1, 2]. The International Program for Chemical Safety (IPCS) of the World Health Organization has made several recommendations. Polybrominated diphenyls production (France) and use should be limited because of the concern over high persistency, bioaccumulation and potential adverse effects at low levels. There is limited toxicity data on deca- and octabromodiphenyls. Commercial use should cease unless safety is demonstrated. For the polybrominated diphenyl oxides, a Task Group felt that polybrominated dibenzo furans, and to a lesser extent the dioxins, may be formed. For decabromodiphenyl oxide, appropriate industrial hygiene measures need to be taken and environmental exposure minimized by effluent and emission control. Controlled incineration procedures should be instituted. For octabromodiphenyl oxide, the hexa and lower isomers should be minimized. There is considerable concern over persistence in the environment and the accumulation in organisms, especially, for pentabromodiphenyl oxide.

There are no regulations proposed or in effect anywhere around the world banning the use of brominated flame retardants. The proposed EU Directive on the brominated diphenyl oxides is withdrawn. Deca and tetrabromo bis-phenol A as well as other brominated flame retardants meet the requirements of the German Ordinance regulating dioxin and furan content of products sold in Germany.

The European search for a replacement for decabromodiphenyl oxide in HIPS has led to consideration of other bromoaromatics such as Saytex 8010 from Albemarle and a heat-stable chlorinated paraffin from ATOCH EM. The former product is more costly, and the latter, if sufficiently heat stable, lowers the heat distortion under load (HDUL) significantly. Neither approach has been fully accepted.

In September 1994, the US Environmental Protection Agency (EPA) released a final draft of exposure and risk assessment of dioxins and like compounds [3, 4]. This reassessment finds the risks greater than previously thought. Based on this reassessment, a picture emerges that tetrachlorodiphenyl dioxins and related compounds are potent toxicants in animals with the potential to produce a spectrum of effects. Some of these effects may be occurring in humans at very low levels and some may be resulting in adverse impacts on human health. The EPA also concluded that dioxin should remain classified as a probable human carcinogen. The American Industrial Health Council disagrees with EPA's declaration that dioxin is definitely linked to lung cancer and soft-tissue sarcoma [5]. Polymer producers have been seeking non-halogen flame retardants and the search has been successful in several polymer systems. Non-halogen flame retardant polycarbonate/ABS blends are now commercial. They contain triphenyl phosphate or resorcinol diphosphate (RI)P as the flame retardant. Modified polyphenylene oxide (GE's Noryl) has used phosphate esters as the flame retardant for the past 15–20 years and the industry recently switched from the alkylated triphenyl phosphate to RDP. Red phosphorus is used with glass-reinforced nylon 6/6 in Europe and melamine cyanurate is used in unfilled nylon. Magnesium hydroxide is being used commercially in polyethylene wire and cable. The non-halogen solutions present other problems such as poor properties (plasticizers lower heat distortion temperature), difficult processing (high loadings of ATH and magnesium hydroxide), corrosion (red

phosphorus) and handling problems (red phosphorus). In this paper we have tried to look at some new trends in the search of the new ecologically-friendly flame retardants.

Mode of Action of Flame Retardants

The main flame retardant systems for polymers currently in use are based on halogenated, phosphorus, nitrogen, and inorganic compounds (Scheme 1). All of these flame retardant system basically inhibit or even suppress the combustion process by chemical or

POLYMER FLAME RETARDANTS

HALOGENATED FR

PHOSPHOROUS FR PHOSPHATE ESTERS

ANTIMONY OXIDE

Mg HYDROXIDE, ALUMINA TRIHYDRATE,
BORON FR, AMMONIUM POLYPHOSPHATE,
MELAMINES, MOLYBDENUM FR

Ecologically friendly FR

POLYMER-ORGANIC CHAR FORMERS:
PVA, STARCH, GLUCOSE DERIVATIVES,
POLYFUNCTIONAL ALCOHOLS

LOW-MELTING GLASSES AND GLASS-CERAMICS:
 $K_2CO_3 - SiO_2$, $K_2SO_4 - Na_2SO_4 - ZnSO_4$

INTERCALATION STRUCTURES, GRAPHITE

POLYMER MORPHOLOGY MODIFICATION,
POLYPROPYLENE-POLYETHYLENE COMPOSITIONS

SCHEME 1

physical action in the gas or condensed phase. The main process are:

1. Physical process acting by cooling (endothermic process), or by dilution.
(Aluminium and magnesium hydroxides, melamines).
2. Chemical process taking place in the Gas Phase are based on radical chain mechanisms supported by high-energy H and OH radicals. These radical can be removed by chemical species like halogen halides, metal halides and P-containing fragments (flame poisoning).
(Halogenated flame retardants and antimony trioxide).
3. In the Condensed Phase the flame retardants can cause carbonization of polymer material, which protect the "native" polymer against heat and oxygen attack.
(Phosphorous compounds and another intumescent systems.)

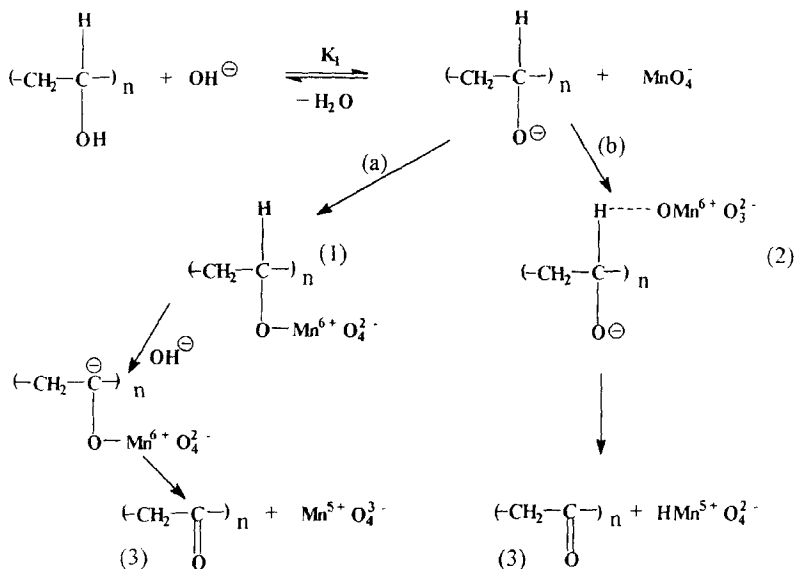
The empirical approach to fire retardance can no longer meet alone the present requirements either in terms of effectiveness or hazard. The above mentioned, commercial the most effective flame retardants so far are halogen, phosphorus, antimony and heavy metal based compounds which however have the most environmental impact either while they perform their action or when burned in incineration of waste containing fire retardant polymeric materials.

The search of new ecologically-friendly flame retardants requires cooperation between industrial and academic research. Much remains to be solved in complete replacement of ecologically harmful flame retardants. This is a problem for many years. It is not our goal today to try to complete that approach, but it's our aim to point out only some new trends in this field. The first example of ecologically-friendly flame retardant system is:

POLYMER-ORGANIC CHAR FORMER

Our recent study [7, 8] has been directed at finding ways to increase the tendency of plastics to char when they are burned. There is a strong correlation between char yield and fire resistance. This follows because 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. It has been studied polymeric

(2), (9):



The reactions (a) and (b) lead to the formation of poly(vinyl ketone) (3) as a final product of oxidation of the substrate.

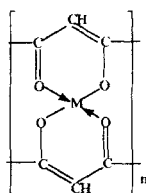
Preliminary Cone tests for PVA and PVA oxidized by KMnO_4 (Tab. II) clearly indicated the substantial improvement of fire resistance characteristics for PVA oxidized by KMnO_4 in comparison with PVA. PVA oxidized by KMnO_4 gives about half the peak of heat release rate (Peak R.H.R. kW/m^2), when compared with pure PVA. Even at 50 kW/m^2 , the yield of char residue for PVA oxidized by KMnO_4 was 9.1%. One reason for this phenomenon may be explained by the ability for PVA oxidized by KMnO_4 - (polyvinyl ketone structures) to act as a neutral (structure 1) and/or monobasic (structure 2) bidentate ligand [7].



TABLE II Cone Calorimeter Data of nylon 6,6-PVA

Material, Heat flux, kW/m^2	Initial wt., g	Char yield, % wt.	Ignition time, sec.	Peak R.H.R., kW/m^2	Total Heat Release, MJ/m^2
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	27.9	30.8	1127	127.6	36.9
$KMnO_4$, 20					
PVA-ox	30.5	12.7	774	194.0	103.4
$KMnO_4$, 35					
PVA-ox	29.6	9.1	18	305.3	119.8
$KMnO_4$, 50					
Nylon 6,6, 50	29.1	1.4	97	1124.6	216.5
Nylon 6,6+	26.4	8.7	94	476.7	138.4
PVA (8:2), 50					
Nylon 6,6+	29.1	8.9	89	399.5	197.5
PVA-ox (8:2)					
$KMnO_4$, 50					

The experimental results of others (IR and electronic spectra) [8] provided 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 $KMnO_4$ indicated the presence of 1.5% of Mn remaining in this polymeric structure. Thus, we suggested 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 $50kW/m^2$ for Nylon 6,6 and PVA (80:20%) compositions (typical rate of heat release curves for each sample is shown in Table I confirmed the assumption of the synergistic effect of carbonization [7]. Each of the individual polymers is less fire resistant

than their composition. The sample with PVA oxidized by KMnO_4 displayed even a better flame retardant properties due to the catalytical effect of Mn-chelate fragments on the formation of char.

Thus, the polymeric char former such as PVA, starch, glucose derivatives a polyfunctional alcohols may present a new trend in the global search for the type of ecologically-safe flame retardant systems.

LOW-MELTING GLASSES

The second example has been developed on the basis of an original concept of a low-melting phases (glasses) as a polymer additives [9, 10].

In principle, low-melting glasses can improve the thermal stability and flammability characteristics of polymers by:

1. Providing a thermal barrier for both undecomposed polymer and the char, if any, which forms as a combustion product.
2. Providing an oxidation barrier to retard oxidation of the thermally degrading polymer and its combustion char residue.
3. Providing a "glue" to hold the combustion char together and give it structural integrity.
4. Providing a coating to cover over or fill in voids in the char, thus providing a more continuous external surface with a lower surface area.
5. Creating the potentially useful components of intumescent polymer additive systems.

W. J. Kroenke been developed a low-melting glass flame retardant system for PVC based on ZnSO_4 - K_2SO_4 - Na_2SO_4 [9]. This system prove to be an excellent char former and a smoke depressant. There were also tested the FR-Low-melting-glasses systems with transition metals: Al, Ca, Ce, Ni, Mn, Co, V.

In the paper of J. Gilman it has been shown that silica gel in combination with potassium carbonate is an effective fire retardant for a wide variety of common polymers (at mass fraction of only 10% total additive) such as polypropylene, nylon, polymethylmethacrylate, poly(vinyl alcohol), cellulose, and to a lesser extent polystyrene and styrene-acrylonitrile [13]. The Cone Calorimeter data indicated that the peak heat release rate is reduced about two times without

significantly increasing the smoke or carbon monoxide levels during the combustion. The efficacy of the additives in each of these inherently non-char-forming thermoplastic polymers (PP, PS, Nylon-6,6 and PMMA) depends on the polymer (PP > Nylon-6,6, PMMA > PS). The authors proposed a mechanism of action for these additives through the formation of a potassium silicate glass during the combustion. The pertinent phase diagrams do not show potassium silicate formation until 725°C. However, if sodium salts are present this temperature drops to 400°C – 500°C. Other work on inorganic glass forming fire retardants examined an analogous borate/carbonate system; B₂O₃/MCO₃. These formulations were found to form an inorganic glassy foam as a surface barrier which insulated and slowed the escape of volatile decomposition gasses [14].

POLYMER MORPHOLOGY MODIFICATION

The last representative of new trend in flame retardation is a modification of polymer physical structure (morphology) by means of polymer-polymer blends. We have found an extremal combustion behavior of a system polypropylene-polypropylene-co-polyethylene [15]. Which can be explained in terms of oxidative degradation of polymer materials. We studied the features of auto-oxidation and combustibility of blends of isotactic polypropylene (PP) and ethylene-propylene copolymers (PP-co-PE) as the thin films (50–80 μ). ASTM D2863 (ISO 4589 Part 2) was used to determine the oxygen index (LOI) for polymer films 140 by 52 mm.

The correlation between a polymer thermal oxidative degradation and its combustion under diffusion flames condition may represent an interesting specific application. In general, the solid phase polymer reaction can play the very important role in reduction of polymer combustibility. If we can decrease the reaction ability of a polymer relatively to an oxygen, the critical conditions of the diffusion flame stability would change. Such a polymer will have a different fire behaviour. The LOI method should be a sensitive one to these transformations.

The kinetics of oxygen consumption for PP/PP-co-PE compositions is shown in Figure 2. It's clearly seen the composition of PP/PP-co-PE (62 : 38) has the highest induction period of autooxidation.

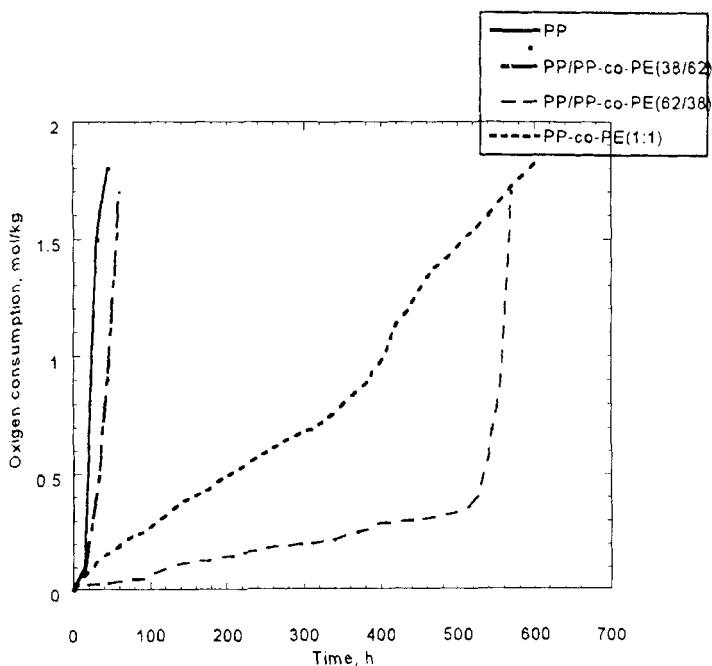


FIGURE 2 Kinetic curves of the oxygen consumption vs. time for PP/PP-co-PE compositions.

In this circumstances it has been proposed a theoretical model of a preliminary oxidation localization in interphaseous zone of a sample [16]. Apparently, the reaction ability of the compositions depends on the chemical structure of the interphaseous zone. It was shown the increase of PP concentration in the PP/PP-co-PE composition from 38 to 62% leads to the lowering of reaction ability of samples. The process of autooxidation begins from the most active ingredient of a polymer composition, PP or PP-co-PE. Interphaseous zone decelerates the polymer oxidation. Otherwise, we simply have a different polymeric system with the different kinetic parameters of an oxidation and different mechanism of the solid phase reactions.

The combustibility tests confirm this hypothesis (Tab. III). The sample with the minimal reaction activity, PP/PP-co-PE (62:38), has the highest values of LOI (21) and the char yield (3.4%).

A correlation between LOI and a char yield for studied polymer compositions is given in Figure 3. This data indicate to the solid phase

TABLE III LOI and char yield for PP/PP-co-PE compositions

Composition	LOI	Char yield, % wt.
PP	17	0
PP/PP-co-PE - 37,5/62,5	19,5	1,5
PP/PP-co-PE - 61,5/38,5	21	3,4
PP-co-PE	18,5	0,5

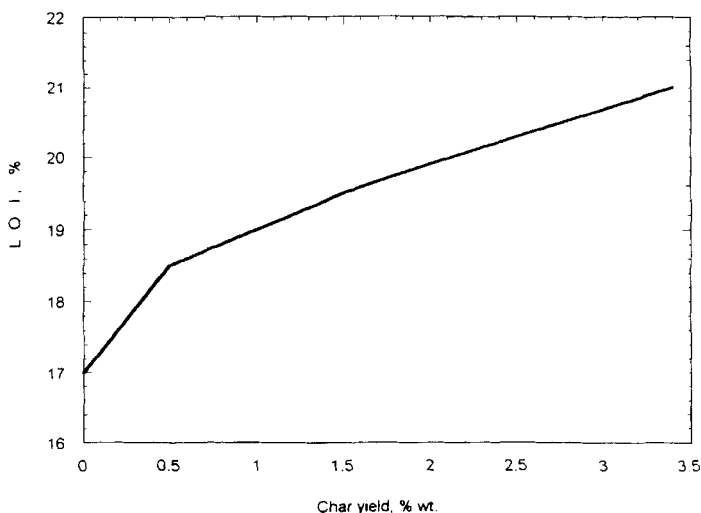


FIGURE 3 LOI vs. char yield for PP/PP-co-PE compositions.

nature of the flame retardancy in PP/PP-co-PE compositions. The morphology modifications in the polymeric system lead to the desirable changes in combustibility.

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