

Photocuring of Acrylate Oligomers Containing Pentabromo Benzylacrylate as Flame-Retarding Monomer and Properties of Cured Films

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ABSTRACT: Photocuring of formulations containing polyurethane and unsaturated polyester acrylate oligomers and a flame-retarding (FR) monomer, that is, pentabromo benzylacrylate, with various α -cleavage-type photoinitiators were studied. The effects of each photoinitiator on photocuring efficiency in both the presence and the absence of the FR monomer were examined. The flame retardancy and both physical and mechanical properties of the cured films were also investigated. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1181–1189, 2002

Key words: flame retardancy; UV-curable polyurethane and polyester acrylate; pentabromo benzylacrylate; photoinitiators

INTRODUCTION

There has been considerable interest in the application of coating systems in various fields. Some of these systems are based on UV-induced polymerizations, in which either of the bifunctional acrylates of epoxy monomers undergo crosslinking by radical or cationic mechanisms, respectively.¹ For indoor or outdoor uses of such materials, it is necessary to protect them from the danger of fire. The nonflammability of UV-cured coatings has therefore been a longstanding requirement.

In earlier investigations for reducing the flammability of polymeric materials, large amounts of metal hydroxide, halogenated, phosphorous-, nitrogen-, and sulfur-containing compounds were

usually added to coatings as flame retardants (FR). However, the addition of a large amount of additive results in changing the mechanical properties of the UV-cured coatings. The incident light may be absorbed by the additives and thus curing efficiency is reduced. Additionally, additives may separate out from the polymer after curing because of incompatibility. In a recent study it was proposed that reactive-type FR monomers could overcome these problems. In this case, bromine-containing monomers in the UV-curable resin converted into a polymer or grafted on the base polymer upon photolysis.^{2,3} Although this study dealt with the flame retardancy and mechanical properties of the cured systems, no correlation with the type of photoinitiator used was attempted. Moreover, the finishing properties of the films such as color and gloss measurements, which are very important in UV-curing applications, were not addressed.

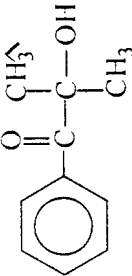
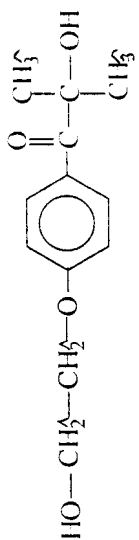
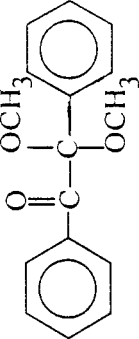
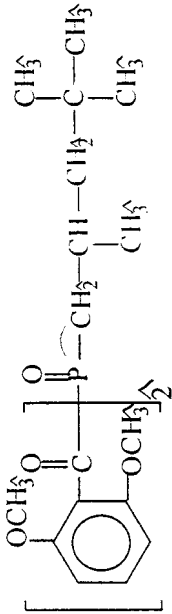
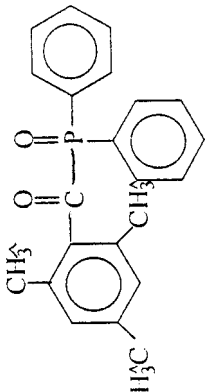
In the present study a model FR monomer, pentabromo benzylacrylate (PBBA), was examined with respect to its influence in UV curing of

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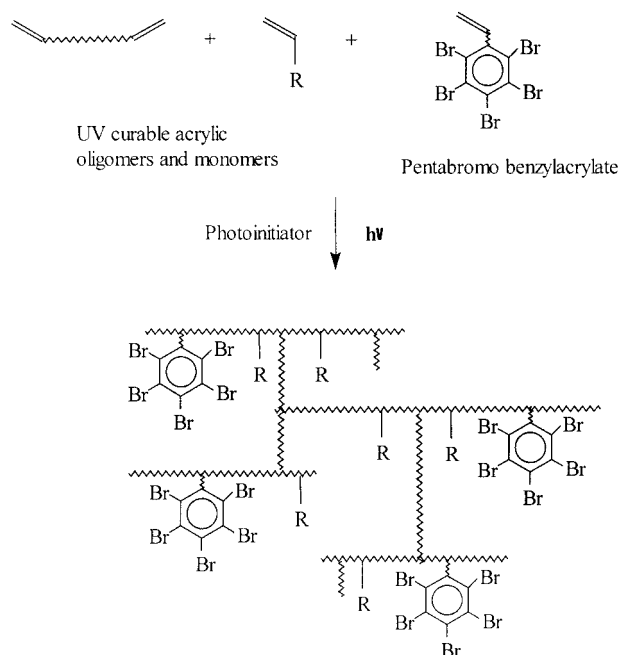
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Table I Characteristics of the Photoinitiators Used in This Study

Photoinitiator	Abbreviation	Trade Name	Absorption Wavelength (nm)	Extinction Coefficient ^a ϵ (L mol ⁻¹ cm ⁻¹)	Structure
2-Hydroxy-2-methyl-phenyl propan-1-one	HMPP	Daracure	265–280 ^b	3.705×10^4	
4-(2-Hydroxyethoxy)phenyl-(2-hydroxy-2-methylpropyl) ketone	HEMP	1173 Irgacure	320–335 ^c 275–285 ^b	5.032×10^4	
2,2-Dimethoxy-2-phenyl acetophenone	DMPA	2959 Irgacure	320–330 ^c 330–340 ^b	4.579×10^4	
Bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide (75% HMPP)	BAPO/HMPP	651 Irgacure	245 ^b	3.075×10^4	
2,2,6-Trimethyl benzoyldiphenyl phosphine oxide (50% HMPP)	TPO/HMPP	1700 Daracure	325 ^c 270–290 ^b	1.446×10^4	

^a Extinction coefficient is calculated in methanol at 254 nm.^b Low concentration 2×10^{-5} g/ml in methanol.^c High concentration 4×10^{-4} g/ml in methanol.



Scheme 1 Photocuring of acrylic oligomers containing pentabromo benzylacrylate.

polyurethane and unsaturated polyester acrylate oligomers by using various photoinitiators. It was of particular interest to establish whether FR monomer can significantly alter the curing trend and the properties of cured coatings. In fact, polymers obtained from PBBA are known to be excellent FR materials because of PBBA's polymeric nature and high bromine content.

EXPERIMENTAL

Materials

The photoinitiators were supplied by Ciba Specialty Chemicals (Switzerland) and used without further purification. The flame-retardant (FR) monomer pentabromo benzylacrylate (PBBA) was a gift from Dead Sea Bromine Group (Israel) and as received. 1,6-Hexanediol diacrylate (HDDA), trimethylol propane triacrylate (TMPTA), and *N*-vinyl pyrrolidone (NVP) were all commercial-grade products from BASF (Germany) and used as received. Styrene (St) (Petkim, Turkey) was purified on an aluminum hydroxide column. Aromatic urethane triacrylate (containing 25 wt % HDDA) and polyester tetracrylate oligomers, sup-

plied from UCB Chemicals (Belgium), were used without further purification.

Preparation and UV Curing of Coatings

Appropriate formulations containing initiator and monomers were thoroughly stirred by using a mechanical stirrer and coated on polished glass plates (5×10 cm) with the aid of a four-sided stainless-steel bar coater. The thickness of the films was about $120 \mu\text{m}$. The samples were then irradiated for given times from a photoreactor consisting of eight TL6 W/08/F6T5 BLB-type UV lamps (Phillips; The Netherlands). The irradiation distance was 30 cm. Retardation attributed to the scavenging effect of oxygen was neglected in this study.

Characterization

The gel content of the UV-cured samples was determined by Soxhlet extraction with acetone

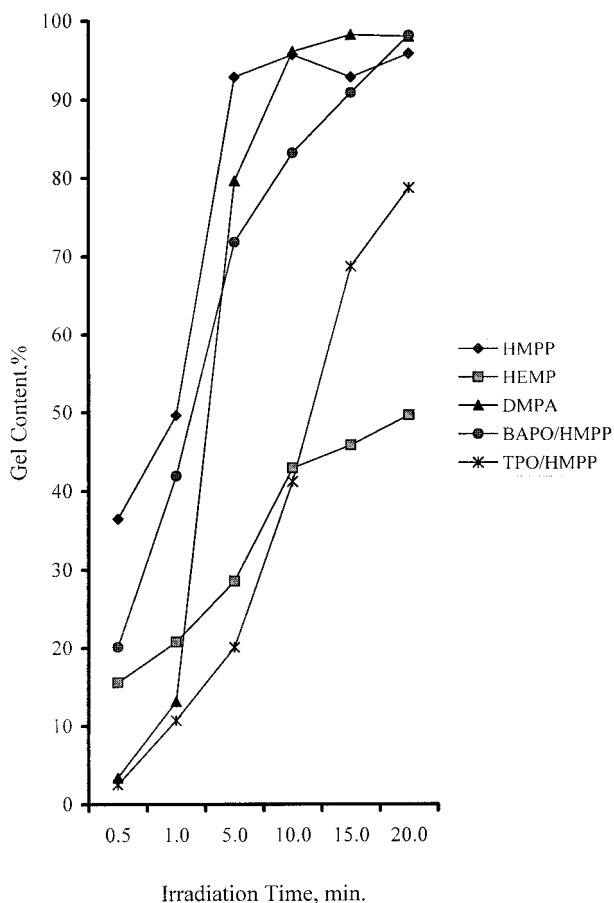


Figure 1 Irradiation time versus gel content curves of cured blank polyurethane resins with various photoinitiators.

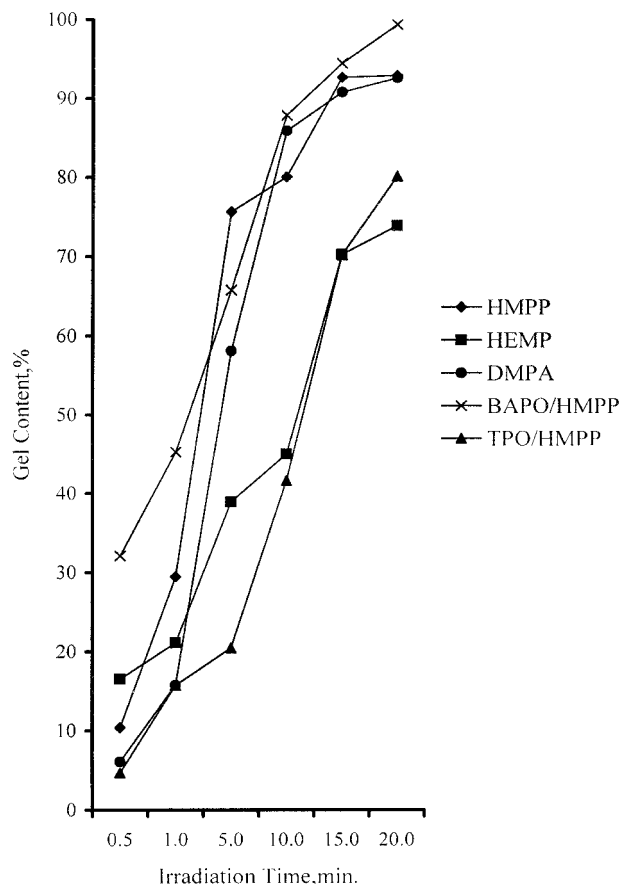


Figure 2 Irradiation time versus gel content curves of cured polyurethane resins containing 3% PBBA monomer with various photoinitiators.

for 24 h. The insoluble gel fraction was dried at 60°C for 48 h and was weighed to calculate gel content.⁴ Thermogravimetric analysis (TGA) was performed on a TG 50 thermogravimetric analyzer (Shimadzu, Japan) with a heating rate of 20°C/min in air. Hardness measurements of the UV-cured samples were conducted using a König–Persöz Hardness Testing device. Strips of cured films (50 × 20 × 3 mm sample dimensions) were cut and tested for tensile properties. The testing was conducted using Zwicky 1120 testing machine. Gloss measurements were performed with a Novo-Glossmeter at 60°. The color of cured films, formed on white cartoons, was determined by Lange spectrophotometer. The limiting oxygen index (LOI) was determined, according to ASTM D2863-95, using a homemade device.⁵ The test samples for all measurements were initially conditioned for 2 h at 25°C and 65% humidity.

RESULTS AND DISCUSSION

The photoinitiators used in this study, represented in Table I together with their structures and trade names, were α -cleavage-type initiators. Upon photolysis these initiators produce two radicals capable of reacting with the olefinic components of the monomers and oligomers to yield an insoluble network according to **Scheme 1**. In this way PBBA was incorporated into the network by chemical bonding. The independent influences of each photoinitiator in the selected compositions containing polyurethane or polyester acrylates, di- and trifunctional monomers, reactive diluent, and FR monomer PBBA on UV curing efficiency were studied. The typical formulation of polyurethane-based UV-curable coating used in this study contained (by weight) 60% urethane acrylate oligomer, 10% TMPA, 15% HDDA, 10% NVP, and 5% photoinitiator.⁶ The monofunctional monomer NVP was replaced with PBA in increasing amounts for the flame-retarding UV-curable formulations.

In the case of unsaturated polyester-based systems, the formulations contained 80% unsaturated polyester oligomer, 15% styrene (St), and 5% HMMP as the photoinitiator. In FR monomer-containing formulations, St monomer was replaced by PBBA.

Irradiation time–gel content curves for the UV curing of urethane acrylate blank and flame-retarding formulations are presented in Figures 1 and 2, respectively. Interestingly, the curves showed similar trends in both systems. In the polyurethane-based system the gel content decreased slightly by using PBBA in the system,

Table II Gloss and Hardness Values of the UV-Cured Films

Photoinitiator	PBBA (%)	Hardness (Persöz)	Gloss (60°)
HMPP	—	110	146
HMPP	3	86	149
HEMP	—	210	150
HEMP	3	207	149
DMPA	—	83	135
DMPA	3	79	133
TPO/HMPP	—	183	147
TPO/HMPP	3	174	143
BAPO/HMPP	—	120	147
BAPO/HMPP	3	115	143

Table III Mechanical and Physical Properties of Polyurethane-Based UV-Cured Films

PBBA (%)	Gel Content (%)	Gloss (60°)	Hardness (Persöz)	Elongation (%)	Tensile Strength (kPa)
0	95.8	146	110	5.2	187
1	83.9	148	107	9	270
2	82.4	148	80	23.6	701
3	81.9	149	86	51	728

indicating that the basic polymer structure of PBBA has a negligible effect on the curing efficiency. The higher crosslinking tendency yields higher hardness values. However, there is a slight decrease in flame-retarding formulations (Figs. 1 and 2, and Table III). Decreases in gel content and hardness values in blank and flame-retarding formulations are similar, an outcome that is taken as a sign that PBBA did not alter the curing efficiency of the photoinitiators.

Notably, HEMP and its combination with TPO are not very effective in photocuring of polyurethane acrylate-based resins. The other three initiators, that is, HMPP, HMPP/BAPO combination, and DMPA, show similar photoinitiating efficiency.⁷ Although DMPA has also been shown to be an efficient initiator for curing of FR formulations, the gloss level of the cured films was rather low (Table II). This behavior may be attributable to the incompatibility of the initiator with the polymerizable oligomeric component. The practical usage of this photoinitiator in such formulations is not suitable, especially when coatings with high gloss level are required. It can be seen from Table III that the presence of FR monomer in the formulations did not change the gloss level of the polyurethane-based cured films. Similar behavior was also observed with the unsaturated polyester-based system (see below).

Table IV Mechanical and Physical Properties of Unsaturated Polyester-Based UV-Cured Films

PBBA (%)	Gel Content (%)	Hardness (Persöz)	Gloss (60°)	Elongation (%)	Tensile Strength (kPa)
0	89.5	270	147	19.6	1080
3	88.9	263	148	14	816
5	90.6	255	142	7.2	458

Table V The Color of Polyurethane-Based Cured Films in Lab System

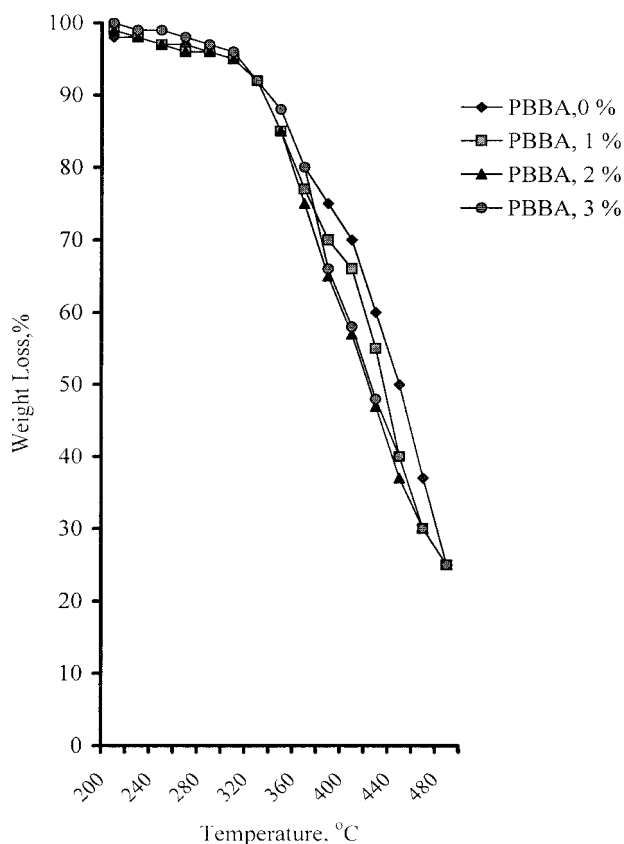
Photoinitiator	PBBA (%)	L ^a	a/-a ^b	b/-b ^c
HMPP	—	92.56	0.28	1.40
HMPP	3	96.24	0.20	2.27
HEMP	—	94.24	-5.82	19.33
HEMP	3	95.93	-5.69	19.55
DMPA	—	96.38	0.38	1.69
DMPA	3	96.24	0.32	2.53
TPO/HMPP	—	92.99	0.35	1.64
TPO/HMPP	3	95.55	0.18	2.37
BAPO/HMPP	—	91.92	-0.06	2.10
BAPO/HMPP	3	94.98	-1.10	5.48

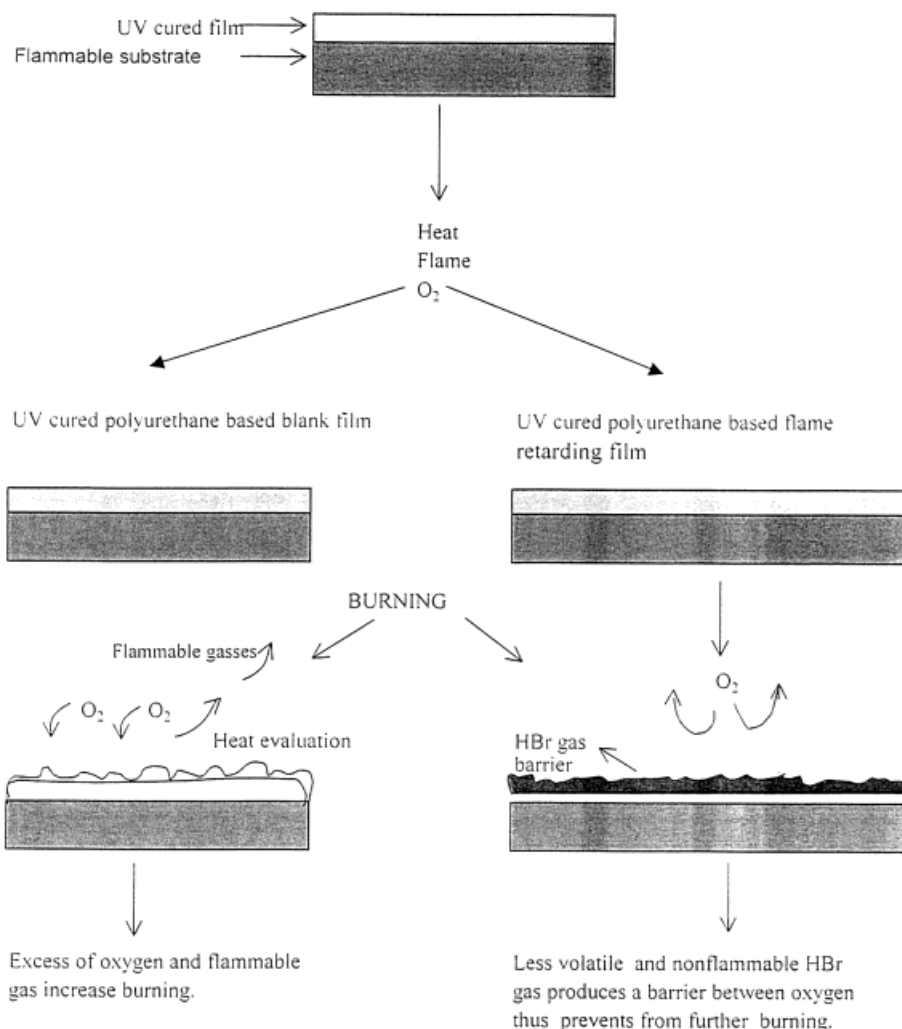
^a L: contrast, brightness.

^b -a: green; a: red.

^c -b: blue; b: yellow.

The effect of PBBA monomer on the mechanical properties of the cured products was studied. In the case of polyurethane-based systems, the


Figure 3 TGA thermograms of cured polyurethane-based resins containing various amounts of PBBA monomer.



Scheme 2 Flame retarding mechanism of PBBA monomer in polyurethane acrylate-based cured films.

incorporation of PBBA (1–3 wt %) leads to an increase in both tensile strength and elongation values (Table III). The higher tensile strength values of PBBA can be explained by the decrease in gel content values. NVP has a carboamide group that has the ability of augmenting and crosslinking the monomer unit.^{8–12} Therefore a decrease on crosslinking could be seen as an increase in tensile strength and elongation values. This may also be the result of the partial replacement of the more rigid polymer *N*-vinyl pyrrolidone (T_g of the corresponding homopolymer, 175°C) by that of FR monomer (T_g of the corresponding homopolymer, 154°C) in polyurethane-based resins.¹³ The variation of the tensile properties also depended on the gel content and, consequently, on the type of photoinitiator. On the

contrary, tensile strength decreases proportionally by replacing PBBA monomer in the unsaturated polyester-based systems (Table IV). In this case the more rigid monomer PBBA is replaced by styrene monomer (T_g of the corresponding homopolymer, 100°C). The change in tensile properties with introducing FR monomer is also detectable as a parallel change in hardness levels of both types of resins.

Moreover, cured FR formulations display similar yellowing tendencies to those of the untreated formulations, that is, PBBA does not impart yellowing to the cured formulation (Table V). It is assumed that the yellowing tendencies are directly related to the gel content of the cured film and the nature of the photoproducts formed from the photoinitiator molecules that are retained in

Table VI The Limiting Oxygen Index (LOI) Values for UV-Cured Polyurethane-Based Systems

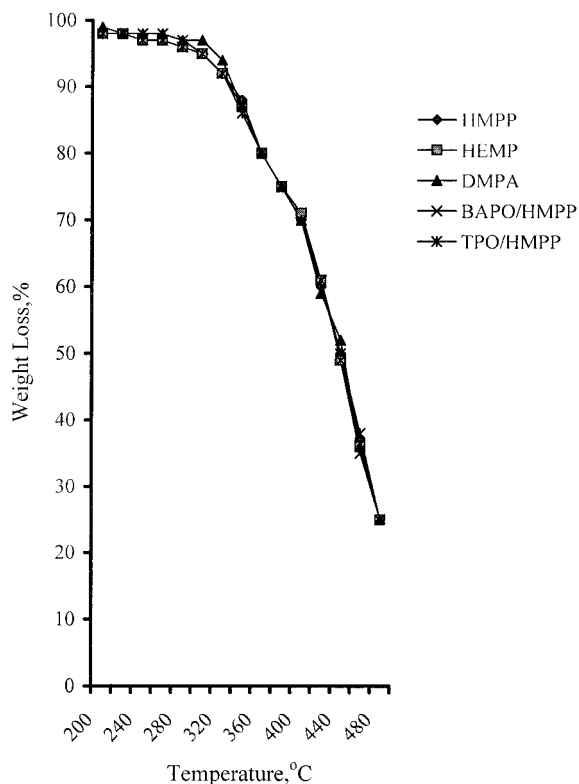
PBBA (%)	LOI (%)
0	17
1	24
2	26
3	32

the cured system.⁷ HMPP and its combination with acylphosphine oxide-type photoinitiators, TPO and BAPO, was shown to give the best performance in a formulation based on acrylated polyurethane resin.¹⁴ In fact, characteristic features of acylphosphine oxide-type photoinitiators include their absorption in the near UV/visible region, no quenching by monomers, and very little yellowing of the cured coatings.

Studies on flame retardancy by means of TGA and LOI and destruction of the UV-cured films containing FR monomer sequences give valuable information about their burning.¹⁵ As can be seen from Figure 3, the thermal stability of cured films is affected by the substitution of FR monomer. The thermal stability of cured resin is slightly reduced by the increasing concentration of PBBA in the formulations. In this stage the expected mechanism of flame retardancy is a replacement of a reactive hydrocarbon radical species required to propagate the combustion by a less-reactive bromine radical. The relatively less volatile and less-flammable bromine-containing compounds that are formed subsequently decompose at elevated temperatures to produce hydrogen bromide, which inhibits oxidation reaction by a radical mechanism similar to that of halides in the combustion of hydrocarbons. Besides this, the action of less-flammable gas in flame control also suggests that barriers are formed between air and

Table VII The Limiting Oxygen Index (LOI) Values for UV-Cured Unsaturated Polyester-Based Systems

PBBA (%)	LOI (%)
0	17
3	33
5	37


Figure 4 TGA thermograms of cured polyurethane-based resins with various photoinitiators.

the flames.² The mechanism of evolving nonflammable gas and preventing propagation of fire is illustrated in **Scheme 2**.

LOI analyses were also performed on the same samples of cured resins. It is known that LOI is related to FR monomer concentration. It also has a linear relationship with the crosslinking density and consequently with the gel content. The oxygen demand to burn the cured resin increases by increasing amounts of FR monomers in the formulation. The accepted limit of oxygen index for covering the self-extinguishing definition of polymers is 26%.¹⁶ From these experimental results (Table VI), the use of 2 wt % PBBA monomer in urethane acrylate-based formulations is sufficient to reduce the flammability characteristics of cured resins. Similar behavior was observed in unsaturated polyester oligomer resins, the results of which are given in Table VII.

The influence of selected combinations of FR monomer and photoinitiators in polyurethane-based resin on thermal behavior and LOI of the cured films was studied. Although there are only slight differences in LOI values in the blank formulations, the TGA curves are all identical (Fig.

4). The type of photoinitiator employed in the system does not affect the thermal degradation of the cured film. However, for flame-retarding formulations, use of the acylphosphine oxides TPO and BAPO as the photoinitiators decreases thermal stability, as can be seen in Figure 5. In the blank formulations the LOI of each photoinitiator (found to be in the range of 17–19%) increased, regardless of the type of photoinitiator used, and reached the value of 32–33% in the presence of FR monomer. The correlation of thermal degradation behavior with the nonflammability was obtained by LOI measurements (Table VIII).

CONCLUSIONS

In conclusion polyurethane and unsaturated polyester-based UV-curable coatings containing FR monomer PBBA can be cured by using various photoinitiators. The resulting crosslinked polymers have significantly higher LOI values than those of untreated ones. These results suggest

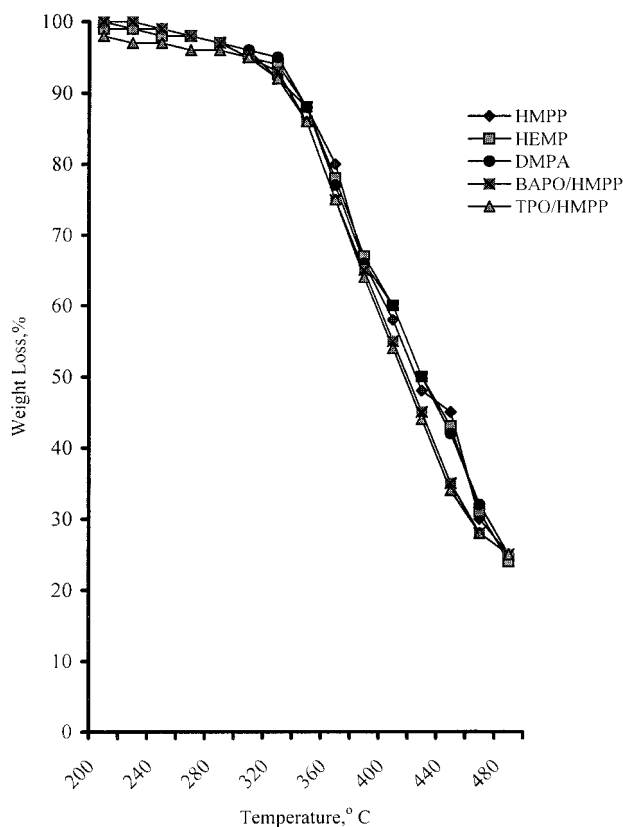


Figure 5 TGA thermograms of cured polyurethane-based resins containing 3% PBBA monomer with various photoinitiators.

Table VIII The Limiting Oxygen Index (LOI) Values for UV-Cured Polyurethane-Based Resins by Using Various Photoinitiators

PBBA (%)	Photoinitiator	LOI (%)
—	HMPP	17
3	HMPP	32
—	HEMP	17
3	HEMP	32
—	DMPA	17
3	DMPA	32
—	TPO/HMPP	19
3	TPO/HMPP	33
—	BAPO/HMPP	19
3	BAPO/HMPP	33

that the flame-retardant chemistry within the UV-cured formulations is complemented by PBBA present in the formulations without influencing photopolymerization chemistry.

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