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UV-curing of Unsatured Polyesters Using Phosphorus Compounds as Photoinitiators

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Abstract : Les composés du phosphore 4-méthoxybenzoildialkylphosphonate (alkyl = méthyl, éthyl) et 4-méthoxybenzoildiphenylphosphine oxyde ont été employés comme des photoamorceurs chez la pólymerisation de certains polyesthères nonsaturés, sous la forme des pellicules. On a étudié l`influence des paramètres suivants sur les propriétés finales de la pellicule : la concentration du photoamorceur, le temps d`exposition, le contenu du pigment, l`épaisseur de la pellicule. On a établi les conditions optime et on a accompli des corrélations des paramètres concentration photoamorceur – contenu du pigment – la dureté pour obtenir des pellicules ayant de très bonnes propriétés.

Abstract: The organophosphorus compounds 4-methoxybenzoyldialkylphosphonate (alkyl = methyl, ethyl) and 4-methoxybenzoyl-diphenylphosphine oxide previously synthesized, were used as photoinitiators for polymerization of unsatured polyesters in order to obtain films. The influence of photoinitiator concentration, exposure time, pigment content on pendulum hardness was studied. The optimal conditions and correlation between photoinitiator concentration-pigment content-pendulum hardness were established.

Keywords: uv-curing, photoinitiators, unsatured polyesters

1. Introduction

Photoinitiated polymerization of the multifunctional monomers and oligomers is one of the most efficient method to produce films based on polymeric materials [1]. These systems undergo rapid transformation of liquid monomer/oligomer into solid polymer simply by exposure to UV radiation in the presence of photoinitiators. The photoinitiators play a key role in UV-curable systems by generating the reactive species, free radicals or ions, able to initiate the polymerization of the multifunctional monomers and oligomers [2]. UV-curing coating systems have advantages such as: good cost/performance relation, low energy consumption, high chemical and mechanical strength of the final coatings, no volatile organic compounds (no solvent), and high speed of the process even at room temperature [3].

Organophosphorus compounds, as acyl-phosphonates and acylphosphine oxides were developed as a new class of photoinitiators. They are very effective in radical polymerization of unsatured monomers (acrylates, styrene, epoxy resins, unsatured polyesters) in order to obtain both transparent and colored coatings [4]. Acylphosphonates and acylphosphine oxides lead to an improved through cure [5]. These photoinitiators can be used either alone or in combination with other photoinitiators, i.e. α-hydroxy ketones (HK) or benzyldimethyl ketal [6], which give a good surface cure [7].

In this paper organophosphorus compounds 4-methoxybenzoyldialkyl phosphonates (alkyl = methyl, ethyl) and 4-methoxybenzoyldiphenylphosphine oxide, previously sinthesized [8], were used as photoinitiators for polymerization of unsatured polyesters, in order to obtain films.

The influence of photoinitiator concentration on film properties was studied.

2. Experimental

The photopolymerizable system contains:

- monomer/oligomer:

unsatured polyesters obtained from ortophtalic acid, maleic acid and polyol, solved in styrene, Azastral 10 and Azastral 60 (provided from Azur SA). Azastral 10 is considered more reactive due to high containing in maleic acid.

- photoinitiators:

4-methoxybenzoyldimethylphosphonate **MBDMP**
4-methoxybenzoyldiethyl phosphonate **MBDEP**
4-methoxybenzoyldiphenylphosphine oxide **MBDPPO**

- additive:

tertiary amine – triethylamine [9].

The photopolymerizable system was laid on glass panel with a film applicator and was exposed to a medium pressure vapour mercury lamp.

The film pendulum hardness of the cured films was determined using Koenig pendulum.

The reactivity of phosphorus containing photoinitiator to unsatured polyesters was performed by photo-DSC method, using a DuPont 930 irradiation unit with a double head differential calorimeter 912 calibrated with indium metal standard. A standard high pressure Hg lamp with 3 mW/cm^2 intensity was used for sample uv exposure.

3. Results and discussion

In Figure 1 and Figure 2 are shown the variation of conversion and polymerization rate versus time using MBDPPO as photoinitiator for Azastral 60 and Azastral 10 polymerization.

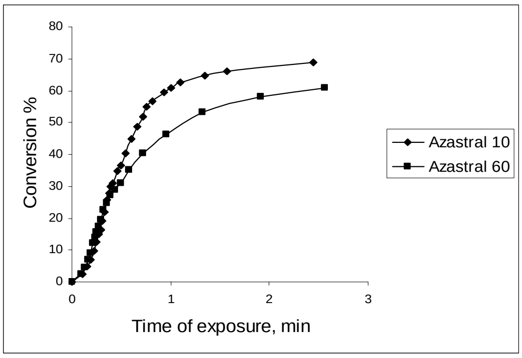

Figure 1. Conversion of Azastral 60 and Azastral 10 in the presence of MBDPPO (concentration 4% w/w and triethylamine concentration 3% w/w)

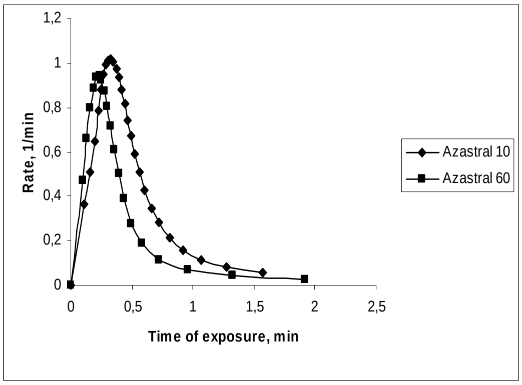

Figure 2. Polymerization rate of Azastral 60 and Azastral 10 in the presence of MBDPPO (concentration 4% w/w and triethylamine concentration 3% w/w)

It can be observed that the conversion is around 70% for Azastral 10 and 60% for Azastral 60, hence the photoinitiator is efficient and can be applied in order to obtain films.

The main property of a UV-cured film is the pendulum hardness, which expresses the crosslink level: high value of pendulum hardness means high crosslinking in polymer. The pendulum hardness is given in seconds and represents the amortization time of an oscilating pendulum on polymeric film and on glass surface. The values of pendulum hardness of films based on unsatured polyesters are presented in Table 1, in comparison with the values of films obtained by thermal polymerization in classical conditions, i.e. in the presence of cobalt octoate-methylethyl ketone peroxide. The photoinitiated polymerization occurs at room temperature while polymerization in classical condition occurs at 120^{0}C.

The experimental data show that the films based on unsatured polyesters have very good value for pendulum hardness. The films obtained by UV-curing in the presence of photoinitiators and UV-radiation need only 6 minutes to cure, and the films obtained by classical method need 35 minutes and 120^{0}C temperature. Therefore, in this case, is more advantageous to use UV-light to cure the films.

TABLE I. Pendulum hardness of films based on unsatured polyesters

Photo initiator	Film thickness, μm	Curing time, min	PH	Aspect film
MBDMP	120 300	6 6	244 228	transparent glossy
MBDEP	120 300	6 6	237 223	transparent glossy
MBDPPO	120 300	4 4	260 254	transparent glossy
Thermic initiator: Co octoate-MEK peroxide 120^{0}C	120 300	35 35	140 124	transparent glossy

The influence of photoinitiator concentration on pendulum hardness is presented in Figure 3.

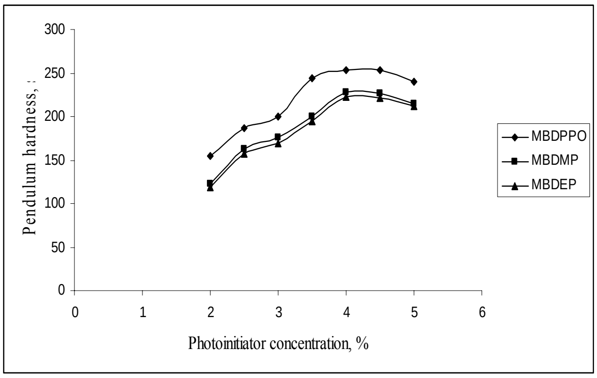

Figure 3. Variation of pendulum hardness with photoinitiator concentration.

The better results of the pendulum hardness were obtained for 4% photoinitiator concentration.

At a concentration higher than 4% the pendulum hardness decreases. This can be explained by competition between the reactions of primary radical with a double bond during the initiation, due to higher concentration of active species, i.e. radicals. At a concetration lower than 2% the film was not cured, the concentration of the formed radicals was not sufficient to assure the crosslinking.

A photoinitiator concentration of 3-4% is usual in practice for acylphosphonates and acylphosphine oxides [10].

The resistance of the obtained films to solvents and chemical agents was studied. The cotton sample with solvent or chemical agents was maintained on the film surface during 30 hours and the modifications appeared on the film were observed. In Table 2 are presented the results.

TABLE 2. The resistance to solvents and chemical agents

Photo initiator	MEK	BA	T	HCl conc	NaOH 50%
MBDMP	A	A	A	A	A
MBDEP	A	B	A	A	A
MBDPPO	A	A	A	A	A

MEK = methylethylketone
BA = butylacetate
T = toluene
A = no deformation
B = low opalescence

The films are very resisting to solvent and chemical agents.

4. Conclusions

The phosphorus compounds 4-methoxybenzoyl-dimethylphosphonate, 4-methoxy-benzoyldiethyl phosphonate and 4-methoxy-benzoyldiphenylphosphine oxide were used succesfuly as photoinitiators for unsatured polyester polymerization in order to obtain UV-cured films.

The pendulum hardness of the UV-cured films are higher than pendulum hardness of the films cured in classical condition, in the presence of cobalt octoate-methylethyl ketone peroxide and at 120^0C.

The influence of the photoinitiator concentration was studied. The best results were obtained for a concentration of 4 % w/w versus monomer.

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