

## STUDY OF THE POLYMERIZATION OF ACRYLIC RESINS BY PHOTOCALORIMETRY

### Influence of initiators and irradiation wavelength

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Due to their advantages from an environmental point of view (i.e. reduction of volatile organic compounds (VOC)), photocurable finishes should be extensively used for industrial wood joinery in the near future. However, several problems are reported, particularly the poor durability of the finishing system. In the present work, the curing reaction of acrylic resins containing some improved photoinitiators was studied by means of photocalorimetry under monochromatic irradiation from 366 to 450 nm. The results show that finishes can be cured even under daylight so that they could be directly applied on site in case of restoration.

**Keywords:** acrylic resins, degree of cure, irradiation wavelength, photocalorimetry, photoinitiators

### Introduction

Due to their advantages from an environmental point of view, photocurable finishes are more and more used in industrial wood joinery and their use should further develop during next years.

Compared to classical polluting solvent-borne systems, waterborne or powder photocurable formulations appear as the solution to respect highly constraining legislation [1, 2].

Indeed UV formulations are composed basically by photoinitiators and a mixture of monomers and/or oligomers dissolved into reactive diluents (i.e. UV curable multifunctional monomers). These latter are then directly involved into the curing process and are 'trapped' into the cured film [3]. Thus using such systems allows to achieve ecofriendly coatings by reducing the emission of volatile organic compounds VOC, from the application of the formulation to the film formation.

Nevertheless some technical problems are reported while using UV photocurable finishes.

On one hand, the photochemical reactivity of some wood components with radical species induces some retardation and inhibition effects during the initiation phase of the curing process. The choice of suitable photochemical initiators can enable the control of these effects [4–6]. Besides the reactivity of wood components has also an influence onto the degree of cure and the mechanical properties of the finish film [7].

On the other hand, the absence of UV absorbers in the formulations and consequently in the cured coating does not allow to achieve a sufficient durability of the protecting system, particularly for outdoor joinery which is submitted to severe climatic conditions. This main drawback explains why wood material is so harshly competed by some more durable materials such as aluminium and PVC.

Thus solutions have to be found in order to make the restoration of wood joinery easier.

Our aims are to develop photocurable formulations containing specific photoinitiators able to initiate the curing process under visible light. In this case, restoration of wood joinery could be done directly on site under daylight and the application of photocurable finishes should become as easy as the one of classical polluting formulations (brushing, spraying).

Moreover, UV absorbers could be incorporated into the formulations in order to enhance the durability of the protection without interacting with the initiation phase of the curing process.

In this study, the photopolymerization of acrylic monomers generally used in commercial formulations of wood finishes was investigated by means of photocalorimetry. The initiation was achieved with an original and complex initiating system able to absorb in the visible domain [8]. The influence of irradiation wavelength onto the curing kinetics was studied by scanning from the UV to the visible part of the light spectrum.

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## Experimental

### Materials

The resins used in this study are acrylate oligomers furnished by UCB Chemicals. Their trade names are: Ebecryl 284 (diacrylic aliphatic polyurethane), Ebecryl 264 (triacrylic aliphatic polyurethane) and Ebecryl 605 (epoxy diacrylate).

Phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide BAPO (97%), isopropylthioxanthone ITX (97%) and N-methyldiethanolamine MDEA (>99%) – defined as ‘2<sup>nd</sup> generation initiators’ – were studied because they show an absorption band which overlaps the visible domain. They were purchased from ALDRICH and used as received without any further purification. Their choice was based upon a study carried out in collaboration with the department of general photochemistry of the ENS Chimie from Mulhouse the results of which showed that these compounds can absorb in the visible domain and can initiate radical processes [9, 10].

The quantities of BAPO, ITX and MDEA were fixed at 0.2, 0.2 and 0.5% mass/resin respectively in the four initiating systems tested i.e. BAPO, BAPO/MDEA, BAPO/ITX/MDEA or ITX/MDEA.

### Methods

#### UV-Vis spectroscopy

The absorption spectra of the different initiating systems studied were recorded using a spectrometer Lambda 16 Perkin Elmer. In order to obtain some comparable results with those obtained with DPC, some precautions have to be taken when using this technique. Indeed, the thickness of the film cured in the DPC crucible is estimated around 100  $\mu\text{m}$ . Now the optical path of the quartz cell used is 1 cm i.e. 100 times greater. Thus the concentration of the different components in the initiating systems has to be divided by 100 and is thus equal to  $4.78 \cdot 10^{-5}$ ,  $7.86 \cdot 10^{-5}$  and  $4.19 \cdot 10^{-4}$  mol L<sup>-1</sup> for BAPO, ITX and MDEA respectively. Note: for these experiments, the resin was replaced by a solvent: tetrahydrofuran (THF)

#### Photocalorimetry

The apparatus is a Differential scanning PhotoCalorimeter (DPC). It consists in a power compensated differential scanning calorimeter DSC7 Perkin Elmer fitted with an irradiation device.

The light source is a Xenon lamp (XBO 450W) with a very large spectrum covering UV to IR domains. Thus the DPC apparatus is fitted with some ‘heat absorption’ devices which are placed on the light path to remove IR wavelengths and avoid a temperature increase on the cells [11, 12].

## Experimental

All the formulations prepared were tested under a monochromatic irradiation at 366, 420, 440 and 450 nm. These wavelengths were selected with a monochromator with a precision of  $\pm 10$  nm.

Prior to the analysis, each mixture was prepared and homogeneously mixed.

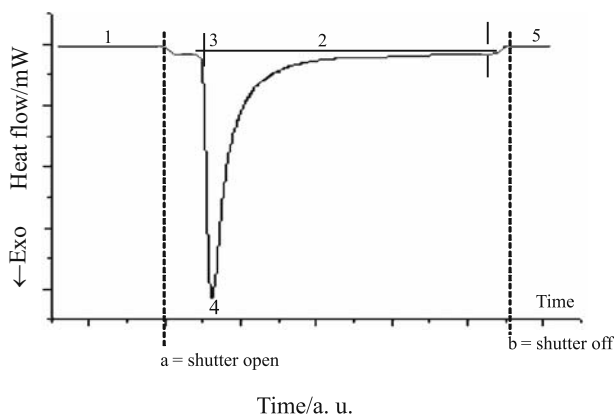
A small quantity (i.e. 11.0 to 12.5 mg accurately weighed) of each system was introduced in a 50  $\mu\text{L}$  aluminium crucible which was placed in the sample compartment of the DSC oven; an empty crucible was used in the reference compartment.

The DSC oven was then purged by a 35 mL min<sup>-1</sup> nitrogen flow to avoid inhibiting effect due to the presence of oxygen onto radical curing process and the temperature was maintained at 25°C. The shutter was open two minutes and half after the introduction of the sample and the duration of the analysis was fixed at 5 min.

On Fig. 1 is given an example of a curve obtained from the procedure described just above.

From the thermal profile recorded in isothermal mode at 25°C, some characteristic values were determined:

- The  $t_{\text{onset}}$  which corresponds to the induction time
- The  $t_{\text{ex}}$  which corresponds to the peak maximum
- The difference  $\Delta t = t_{\text{ex}} - t_{\text{onset}}$  that quantifies the system reactivity at the beginning of the polymerization
- The global enthalpy ( $\Delta H_g$ ) that quantifies the curing degree for the resin at the end of the reaction.



**Fig. 1** Example of a thermogram showing an exothermal peak of photopolymerization (irradiation from a to b, 1 and 5=baseline in absence of irradiation, 2=baseline under irradiation, 3= $t_{\text{onset}}$ , 4= $t_{\text{ex}}$ )

## Results and discussion

The main photoinitiators used in classical photocurable formulations absorb in the near UV domain due to transitions  $n \rightarrow \pi^*$ . That is why medium pressure mercury vapor lamps which have a very in-

tense band at 366 nm are so frequently implemented to polymerize these resins.

Thus in a first part of our study, the curing reaction of the oligomers was performed under monochromatic excitation at 366 nm in order to compare our initiating systems with photoinitiators of '1<sup>st</sup> generation' [6].

*Photocalorimetric analysis of the curing reaction underwent by the Ebecryl oligomers at 366 nm*

Whatever the photoinitiating system used, the polymerization of the three oligomers took place as confirmed by the polymerisation enthalpies measured. Indeed the polymerization enthalpy of these resins alone is expected to be around 200 J g<sup>-1</sup>. For example, Ruiz *et al.* [13, 14] determined the polymerization enthalpy by DPC for Ebecryl 270 (diacrylic aliphatic polyurethane the structure of which is nearly equivalent to Ebecryl 284) initiated by Darocur 1173 photoinitiator and found a value of 191.5 or 208 J g<sup>-1</sup> depending on the amount of resin or thickness of the coating tested.

We also can estimate theoretically these polymerization enthalpies by referring to a formula given in a recent article by Bayou *et al.* [15].

$$\Delta H_{\text{theo}} = (1/M)Ef$$

where *M* is the molar mass of the oligomer, *E* is the required energy to break double bond of acrylate functions and is equal to 86.1 kJ mol<sup>-1</sup> and *f* is the oligomer functionality (e.g. 2 for Ebecryl 284 and 3 for Ebecryl 264).

The application of this equation gives theoretical values of 143.5 and 215.5 J g<sup>-1</sup> for Ebecryl 284 and 264, respectively.

Initiation by BAPO

The irradiation at 366 nm allows a fast polymerization of the three oligomers in presence of BAPO. The variation of the partial enthalpy  $\Delta H(t)$  as a function of time (Fig. 2) shows that the curing kinetics are of the same order at the beginning of the reaction. But a more refined analysis of the thermograms enlightens different behaviours (Table 1).

Despite a higher functionality (three acrylic functions), Ebecryl 264 is less reactive (highest  $\Delta t$ )

**Table 1** Photocuring initiated by BAPO at 366 nm

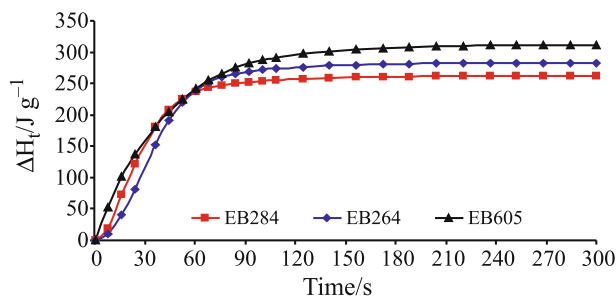
Ebecryl	<i>t<sub>ex</sub></i> / min	<i>t<sub>onset</sub></i> / min	$\Delta t = t_{\text{ex}} - t_{\text{onset}}$ / min	$\Delta H_g$ / J g <sup>-1</sup>
284	0.18	0.04	0.14	179.8
264	0.51	0.02	0.49	194.2
605	0.08	0.02	0.06	229.5

than diacrylic oligomers. The most reactive Ebecryl 605 leads to the highest curing degree (highest  $\Delta H_g$ ) whereas the curing degrees observed with Ebecryl 264 and 284 are nearly equivalent.

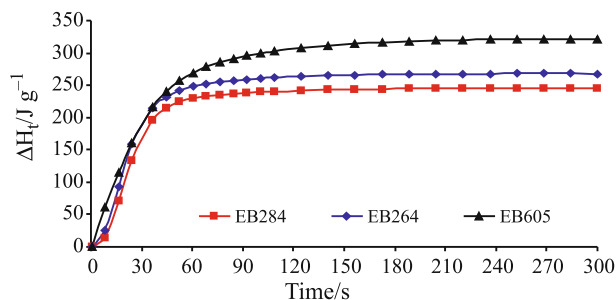
Initiation by the system BAPO/MDEA

As it can be seen in Fig. 3, the addition of the amine does not modify the curing kinetics of the oligomers 284 and 605. On the other hand, its presence improves the curing reaction of the oligomer 264 (Table 2). The global enthalpy measured and the reactivity of the system is higher for this oligomer.

The way the BAPO is decomposed is based on a mechanism involving a bond rupture – this reaction is very fast since the lifetime of the triplet state <sup>3</sup>[BAPO] is very short – the presence of the amine does not modify the initiation step of the polymerization. Indeed we observe on Figs 2 and 3 that the reaction kinetics are nearly the same for both 284 and 605 oligomers. With Ebecryl 264, the value of *t<sub>ex</sub>* (time required to observe the peak maximum) is decreased in presence of the amine. It is well known that the addition of a tertiary amine in photocurable resins reduces the inhibiting effect due to oxygen. The main drawback of such an addition is the change of coloration (yellowing) of the finishing system when exposed in outdoor conditions. For example, this effect is clearly observed in the case of clear finishes applied onto pale woods as spruce.



**Fig. 2** Curing reaction of oligomers photoinitiated by BAPO. Wavelength 366 nm



**Fig. 3** Curing reaction of oligomers photoinitiated by BAPO/MDEA. Wavelength 366 nm

**Table 2** Photocuring initiated by BAPO/MDEA at 366 nm

Ebecryl	$t_{\text{ex}}/\text{min}$	$t_{\text{onset}}/\text{min}$	$\Delta t = t_{\text{ex}} - t_{\text{onset}}/\text{min}$	$\Delta H_g/\text{J g}^{-1}$
284	0.29	0.05	0.24	169.5
264	0.26	0.03	0.23	187.5
605	0.08	0.02	0.06	234.2

The incorporation of the amine (MDEA) does not significantly modify the curing degrees measured at the end of the reaction.

#### Initiation by a mixture ITX/MDEA

This initiating system enables to cure the three oligomers in quite equivalent conditions as those obtained with an initiation by BAPO (Fig. 4). Ebecryl 605 is again the more reactive oligomer but with this initiating system Ebecryl 264 tends to have the same behaviour.

The curing rates achieved are of the same order as those measured for the reaction in the presence of BAPO (Table 3).

Since the photocalorimeter used in this study allows to choose a monochromatic wavelength of irradiation, we can discuss the influence of wavelength onto the curing characteristics for the three oligomers studied.

#### *Influence of the irradiation wavelength onto the photocuring reaction*

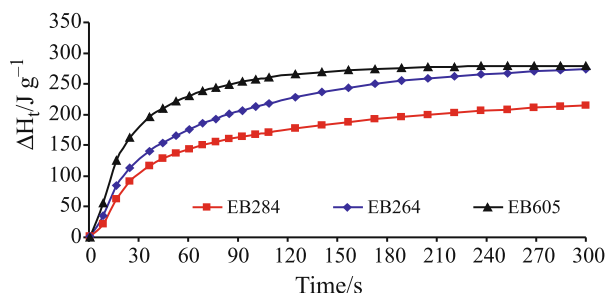
##### Initiation by ITX/MDEA

The results obtained at 420, 440 and 450 nm irradiation wavelengths are given in Table 4.

From the results obtained, it appears that the reactivity of the formulations is greatly decreased as the wavelength is increased. Also only Ebecryl 605 is able to polymerize at 450 nm. It is noteworthy that the quantity of photons absorbed by the reactive medium is very low at these wavelengths because it corre-

**Table 3** Photocuring initiated by ITX/MDEA at 366 nm

Ebecryl	$t_{\text{ex}}/\text{min}$	$t_{\text{onset}}/\text{min}$	$\Delta t = t_{\text{ex}} - t_{\text{onset}}/\text{min}$	$\Delta H_g/\text{J g}^{-1}$
284	0.16	0.03	0.13	153.6
264	0.11	0.02	0.09	196.0
605	0.11	0.01	0.10	209.3

**Fig. 4** Curing reaction of oligomers photoinitiated by ITX/MDEA. Wavelength 366 nm

sponds to the extremity of the absorption band. The same observations are done as the curing degree is concerned: it decreases as the wavelength increases.

Nevertheless, we can conclude that all studied oligomers cure at a 420 nm irradiation wavelength (i.e. visible).

In order to find potential synergetic effects between the different initiating systems (based on mechanisms of rupture and hydrogen transfer), the same methodology was implemented for reactions initiated by BAPO/ITX/MDEA.

##### Initiation by BAPO/ITX/MDEA

The results obtained are given in Table 5. The addition of BAPO does not modify the curing kinetics observed with ITX/MDEA at 366 nm. But in the visible domain, the system BAPO/ITX/MDEA allows the polymerization of the three oligomers even at 450 nm with quite high curing degrees. As it can be observed,

**Table 4** influence of the irradiation wavelength onto the curing reaction initiated by an ITX/MDEA mixture

Wavelength/nm	Ebecryl	$t_{\text{ex}}/\text{min}$	$t_{\text{onset}}/\text{min}$	$\Delta t = t_{\text{ex}} - t_{\text{onset}}/\text{min}$	$\Delta H_g/\text{J g}^{-1}$
420	284	0.54	0.17	0.37	69.2
	264	0.75	0.07	0.68	142.4
	605	0.29	0.05	0.24	200.6
440	284	—	—	—	—
	264	3.90	3.1	0.8	129.8
	605	3.35	2.68	0.67	133.8
450	284	—	—	—	—
	264	—	—	—	—
	605	3.36	2.72	0.64	108.9

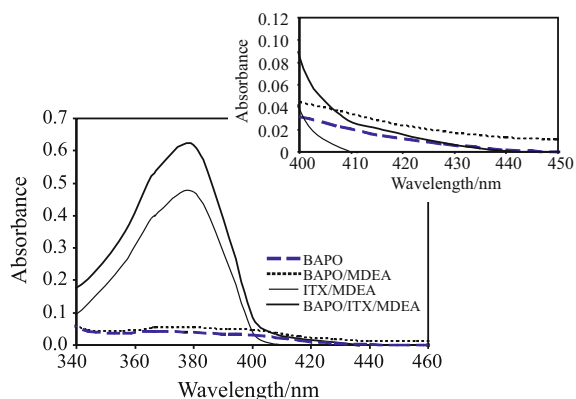
The symbol — means that no reaction occurred at the wavelength considered

**Table 5** Influence of the wavelength onto the photocuring initiated by a BAPO/ITX/MDEA mixture

Wavelength/nm	Ebecryl	$t_{\text{ex}}/\text{min}$	$t_{\text{onset}}/\text{min}$	$\Delta t = t_{\text{ex}} - t_{\text{onset}}/\text{min}$	$\Delta H_g/\text{J g}^{-1}$
366	284	0.16	0.03	0.13	157.9
	264	0.10	0.02	0.08	198.8
	605	0.09	0.01	0.08	200.6
420	284	0.22	0.04	0.18	169.4
	264	0.35	0.02	0.33	175.9
	605	0.20	0.04	0.16	230.3
440	284	4.23	2.76	1.47	147.5
	264	2.77	2.57	0.20	167.9
	605	2.78	2.56	0.22	193.4
450	284	5.29	2.57	2.72	116.9
	264	3.27	2.76	0.51	162.6
	605	3.09	2.65	0.44	139.2

Ebecryl 264 has a particular behaviour: its curing rate does not significantly change as the wavelength in the visible domain is changed.

The UV-visible absorption spectra of both initiating systems ITX/MDEA and BAPO/ITX/MDEA shown on Fig. 5 confirm these results. Indeed we can observe on one hand that the ITX/MDEA system absorbs slightly in the visible domain and this absorption is sufficient to cure the three resins for wavelengths till 420 nm. On the other hand, the absorption in the visible domain for the full initiating system is quite large and allows the curing of the three resins even at wavelengths of 450 nm.



**Fig. 5** UV-Vis spectra for initiating systems. The wavelength range between 400 and 450 nm is magnified in the right corner. The concentrations in the systems are equal to  $4.78 \cdot 10^{-5}$ ,  $7.86 \cdot 10^{-5}$  and  $4.19 \cdot 10^{-4}$  mol L<sup>-1</sup> for BAPO, ITX and MDEA respectively

## Conclusions

Photocalorimetry appeared as a valuable tool to study the curing reaction of acrylate resins initiated by 2<sup>nd</sup> generation initiators and the results obtained are very

promising. Indeed, we observed that the photosensitive systems tested (i.e. simplified formulations which can be used as clear finishing systems for wood) can be cured even under daylight. The application of such photocurable resins could develop in all domains of industrial joinery because the restoration on site becomes possible while conforming to the more and more severe environmental constraints, more particularly those related to the reduction of VOC.

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