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Study of the polymerization of acrylic resins by photocalorimetry: interactions between UV initiators and absorbers

Y. Irmouli · B. George · A. Merlin

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Abstract Photocurable finishes should be extensively used for industrial wood joinery in the near future even if some technical problems have still to be solved and if the durability of the finishing system has to be enhanced. In a previous work, we studied the curing reaction of acrylic resins containing some particular photoinitiators by photocalorimetry and showed that curing can be achieved under daylight with these compounds (i.e. solving the problem of restoration on site). The aim of this work is to enhance the durability of these systems by incorporating UV absorbers into the formulations. The consequences of such an addition onto the curing kinetics are again investigated by photocalorimetry.

Keywords Acrylic resins · Degree of cure · Irradiation wavelength · Mineral and organic UV absorbers · 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 addition of UV absorbers able to delay or inhibit degradation phenomenons [8, 9] is not possible. Their absence 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. Thus solutions have to be found in order to make the restoration of wood joinery easier.

We showed in a previous article [10] that some original and complex initiating systems able to absorb in the visible domain could be used to photocure formulations of wood finishes. 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).

Y. Irmouli · B. George (✉) · A. Merlin
Faculté des Sciences, LERMAB UMR INRA/ENGREF/UHP
1093, Nancy1 Boulevard des aiguillettes, BP 70239, 54506
Vandoeuvre cedex, France
e-mail: Beatrice.George@lermab.uhp-nancy.fr

Our aims now are to study if UV absorbers could be incorporated into these formulations in order to enhance the durability of the protection without interacting with the initiation phase of the curing process.

In this work, the photopolymerization of acrylic monomers initiated by UV–visible initiators previously mentioned in presence of UV absorbers was investigated by means of photocalorimetry to draw the possible interactions between these compounds. The influence of irradiation wavelength onto the curing kinetics was also studied by scanning from the UV to the visible part of the light spectrum.

Experimental

Materials

The resins used in this study are acrylate oligomers furnished by UCB Chemicals. Their trade names are Ebecryl 8402 (aliphatic polyurethane acrylate) and Ebecryl 605 (epoxy diacrylate). They were respectively diluted by 50% and 30% of 1,6-hexanediol diacrylate HDDA.

Phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide BAPO (97%), isopropylthioxanthone ITX (97%) and *N*-methyldiethanolamine MDEA (>99%) were used because they were shown to be efficient in the initiating step of a polymerization process under visible light [10]. They were purchased from ALDRICH and used as received without any further purification. The quantities of BAPO, ITX and MDEA were fixed at 0.2%, 0.2% and 0.5% weight/resin respectively in both initiating systems tested i.e. BAPO/ITX/MDEA or ITX/MDEA.

Three different organic and inorganic UV absorbers were tested. Absorber Tinuvin 1130 is an organic compound based on 2-hydroxyphenyl triazole which was provided by Ciba Specialty Chemicals Inc. Inorganic absorber Rhodigard S100 was furnished by Rhodia Electronics and Catalysis as a nanodispersion of cerium oxide with a diameter of particles comprised between 5 and 100 nm. Inorganic absorber Hombitec RM 400 WP was provided by Sachtleben Chimie GmbH and is mainly composed of titanium dioxide TiO_2. Respectively 3%, 2.5% and 1% weight of Tinuvin 1130, Rhodigard S100 and Hombitec RM 400 WP were incorporated into the different formulations.

UV–visible spectroscopy

The absorption spectra of the different absorbers and initiating systems in tetrahydrofuran (THF) solutions were recorded using a spectrometer Lambda 16 Perkin Elmer. The concentration of BAPO, ITX and MDEA was equal to 4.78×10^{-5}, 7.86×10^{-5} and 4.19×10^{-4} mol L^{-1} respectively. For UV absorbers, the concentration was 3%, 2.5% and 1% weight for Tinuvin 1130, Rhodigard S100 and Hombitec RM400 respectively.

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 450 W) 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 conditions

All the formulations prepared were tested in isothermal mode at 25 °C under a monochromatic irradiation at 366, 420, 440 and 450 nm. These wavelengths were selected with a monochromator with a precision of ±10 nm. The samples were also irradiated by using the whole spectrum of the lamp. For some experiments, a filter was intercalated so that only the visible light ($\lambda > 400$ nm) could reach the samples.

Each sample was prepared and the experiment carried out the same way as in our previous work [10]. The exothermal peak obtained was treated to obtain some characteristic values i.e.:

- The t_{onset} which corresponds to the induction time
- The t_{ex} which corresponds to the peak maximum

(The difference $\Delta t = t_{ex} - t_{onset}$ quantifies the system reactivity at the beginning of the polymerization)

- The partial and global enthalpies (ΔH_t and ΔH_g) that give the curing degree of the resin at different times and at the end of the reaction.

Results and discussion

First the curing reaction of the oligomers was performed under monochromatic excitation at 366 nm because in industrial joinery medium pressure mercury vapor lamps which have a very intense band at 366 nm are very frequently implemented to polymerize photocurable formulations. Indeed the main photoinitiators used in classical finishing systems absorb in the near UV domain due to transitions $n \rightarrow \pi^*$.

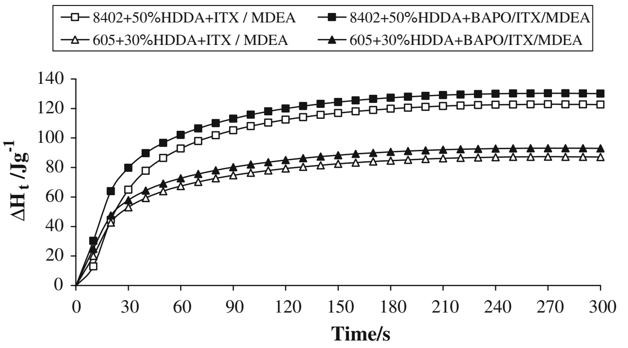


Fig. 1 Curing reaction of both oligomers with both initiating systems at a wavelength of 366 nm

The Fig. 1 shows the curing reaction of both resins at 366 nm with ITX/MDEA and BAPO/ITX/MDEA initiating systems

The triplet state of the thioxanthone ^{3}[ITX] contributes to the reaction of photoreduction by pulling out a H-atom from the amine MDEA used as a co-initiator. Only one of both radicals generated is able to initiate the curing process i.e. the aminyl radical.

Even if the decomposition of BAPO -based on a mechanism involving a homolytic bond rupture-leads to the formation of two radicals, its addition into the preceding initiating system does not modify greatly the polymerization. It only decreases slightly the induction times (t_{onset} and t_{ex} lower) and increases ΔHg values of 4% (cf. Table 1). This is probably due to a filter effect imposed by ITX/MDEA relative to BAPO. At 366 nm, the photons are mainly absorbed by chromophores from ITX/MDEA and at this wavelength the molar absorption coefficient for this system is 6 times greater than for BAPO.

The values of the overall enthalpy ΔHg for both resins are a little bit smaller than those reported in our previous work and also elsewhere [13, 14]. For these experiments, oligomers were diluted into HDDA. This addition contributed to this decrease of ΔHg but also to the improvement of the mechanical properties of the finishing film. Now these characteristics are of a great interest from an applied point of view. The film achieved in this case is less brittle than in absence of diluent and fewer cracks appear during the ageing of the system (results not shown here).

The results obtained by varying the irradiation conditions at 420, 440 and 450 nm, with the whole or the sole visible part of the spectrum) are also given in Table 1 for both resins.

From the results obtained, it appears that whatever the initiating system implemented, the reactivity of the formulations greatly decreased i.e. the $\Delta t = t_{ex} - t_{onset}$ increased as the wavelength of the monochromatic irradiation increased. It is noteworthy that the quantity of photons absorbed by the reactive medium is very low at these wavelengths because it corresponds to the extremity of the absorption band for the photoinitiator. The same observations are done as the curing degree is concerned: it decreases as the wavelength increases but the highest values are obtained at 420 nm. By using the visible part of the light, and of course the whole spectrum, the reactivity and the curing degree are greatly improved since the quantum yield is enlarged.

As already mentioned, the addition of BAPO does not significantly increase the curing degree (less than 10%) but tends to accelerate the reaction and improve the curing kinetics observed with ITX/MDEA.

Table 1 Influence of the irradiation wavelength onto the curing reaction initiated by a ITX/MDEA and BAPO/ITX/MDEA

Wavelength (nm)	ITX/MDEA				BAPO/ITX/MDEA			
	t_{ex} (min)	t_{onset} (min)	Δt (min)	ΔH_g (Jg^{-1})	t_{ex} (min)	t_{onset} (min)	Δt (min)	ΔH_g (Jg^{-1})
Ebecryl 605 + 30% HDDA								
366	0.12	0.02	0.10	136.75	0.10	0.01	0.09	142.34
420	0.12	0.02	0.10	281.70	0.13	0.03	0.10	293.12
440	0.23	0.04	0.19	225.06	0.14	0.02	0.12	238.98
450	0.37	0.04	0.33	155.72	0.26	0.05	0.21	166.08
Filter 400 nm	0.15	0.01	0.14	510.07	0.07	0.01	0.06	502.79
All spectrum	0.08	0.01	0.07	625.95	0.07	0.01	0.06	581.49
Ebecryl 8402 + 50% HDDA								
366	0.19	0.04	0.15	173.97	0.12	0.03	0.09	181.90
420	0.26	0.04	0.22	260.71	0.21	0.05	0.16	284.84
440	0.56	0.05	0.51	219.58	0.33	0.05	0.28	253.30
450	0.85	0.07	0.78	211.81	0.41	0.09	0.32	229.15
Filter 400 nm	0.09	0.02	0.07	484.78	0.09	0.02	0.07	497.15
All spectrum	0.07	0.01	0.06	584.82	0.09	0.01	0.08	597.27

Study of the interactions between the initiating systems and UV absorbers

It is noteworthy that the initiators used have an absorption spectrum shifted towards higher wavelengths ($\lambda > 400$ nm) as it can be observed on Fig. 2. Also they are assumed to remain efficient even if some UV absorbers are added into the formulations.

The variation at 366 nm of the partial enthalpy ΔH(t) as a function of time is shown on Figs. 3, 4 for ebecryl 8402 + 50% HDDA in presence of absorbers and ITX/MDEA or BAPO/ITX/MDEA as initiating system

Whatever the photoinitiating system used, the polymerization of the oligomer at 366 nm took place even in presence of UV absorbers as confirmed by the polymerisation enthalpies measured. Nevertheless, the polymerization kinetics are noticeably affected as well as the degree of cure. The three absorbers nearly behave the same as ITX/MDEA is used as initiating system. Indeed the curves giving the variation of enthalpy as a function of time are almost superimposed. For the complete system BAPO/ITX/MDEA, the effect of absorbers can be distinguished: the inhibition phenomenon increases as organic absorber tinuvin 1130 is used compared to inorganic ones hombitec and rhodigard (the same observation for resin ebecryl 605 with both initiating system).These results can be explained by a high absorption rate of UV absorbers at this wavelength that precludes the photon absorption by photoiniators.

In the following part of the article, we only present the results concerning the resin ebecryl 8402 initiated by BAPO/ITX/MDEA because this case gives a good picture of the overall studied systems.

As the irradiation wavelength is increased (experiments at 420, 440 and 450 nm), again the values of ΔHg first increased compared to those at 366 nm before decreasing (cf. Fig. 5).

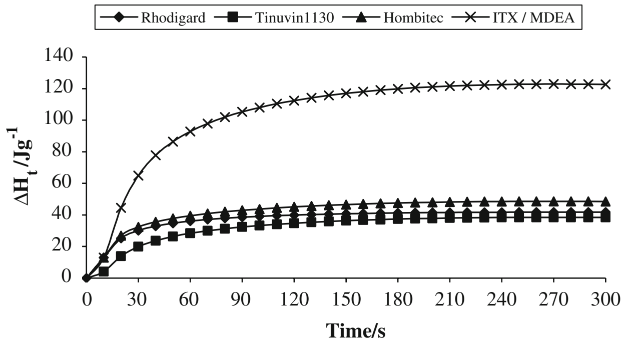


Fig. 3 Curing reaction of ebecryl 8402 + 50% HDDA photoinitiated by ITX/MDEA in presence of absorbers. Monochromator at 366 nm

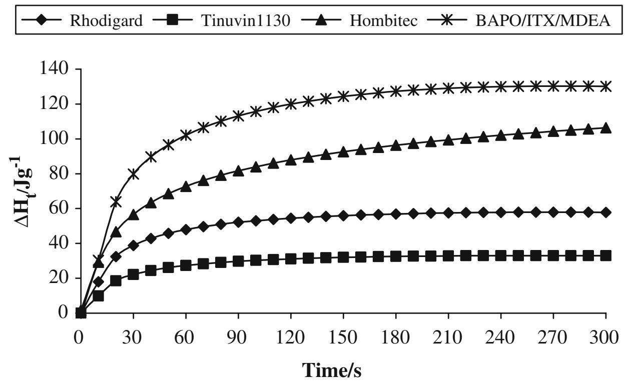
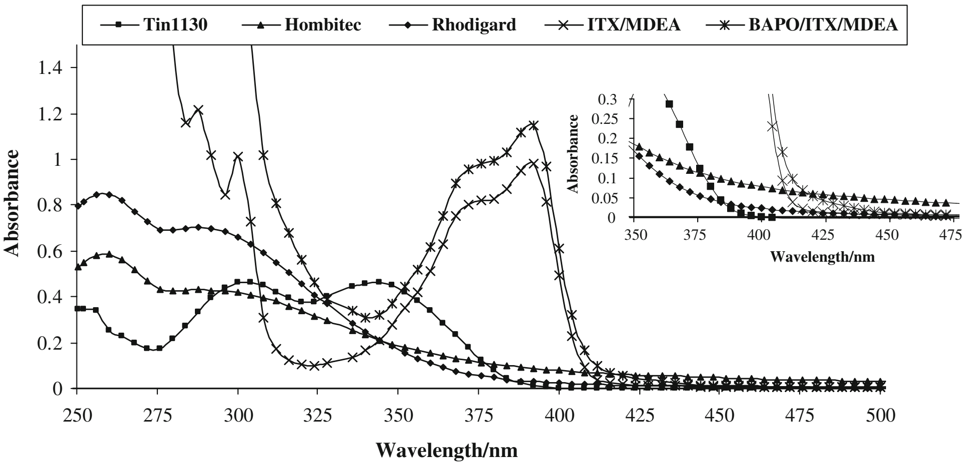


Fig. 4 Curing reaction of ebecryl 8402 + 50% HDDA photoinitiated by BAPO/ITX/MDEA in presence of absorbers. Monochromator at 366 nm

The effect of UV absorbers onto ΔHg can be considered as no significant onto the polymerization of Ebecryl 8402 + 50% HDDA initiated by BAPO/ITX/MDEA under visible monochromatic wavelengths. The differences between the control values and those for experiments with UV absorbers are generally less than 10% excepted for two experiments with Tinuvin and Hombitec (cf. Fig. 6).

Fig. 2 UV–visible spectra for initiating systems and UV absorbers used. The concentrations are equal to 4.78×10^{-5}, 7.86×10^{-5} and 4.19×10^{-4} mol L^{-1} for BAPO, ITX and MDEA respectively. Tinuvin, rhodigard and hombitec were used at 3%, 2.5% and 1% weight



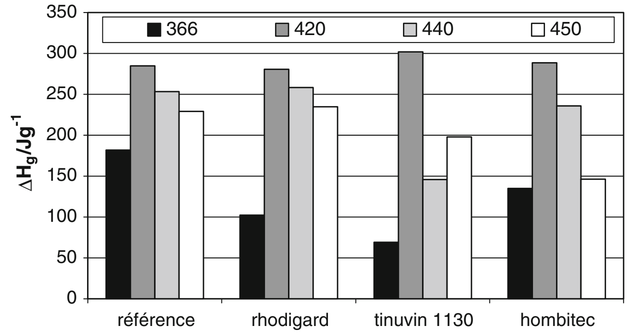


Fig. 5 Evolution of the overall enthalpy ΔH_g at different monochromatic wavelengths in presence or absence of UV absorbers (system Ebecryl 8402 + 50% HDDA initiated by BAPO/ITX/MDEA)

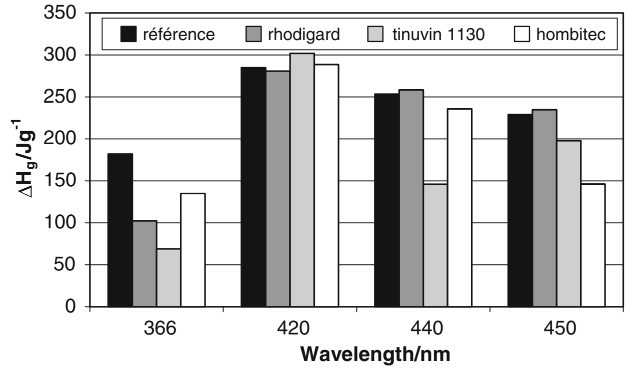


Fig. 6 Effect of the UV absorbers onto the evolution of the overall enthalpy ΔH_g as a function of wavelength (system Ebecryl 8402 + 50% HDDA initiated by BAPO/ITX/MDEA)

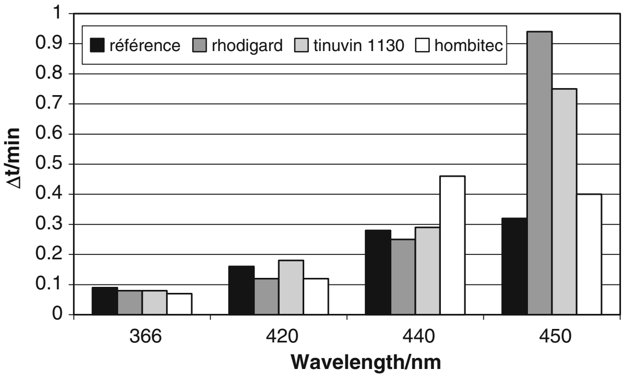


Fig. 7 Effect of the UV absorbers onto the reactivity as a function of wavelength (system Ebecryl 8402 + 50% HDDA initiated by BAPO/ITX/MDEA)

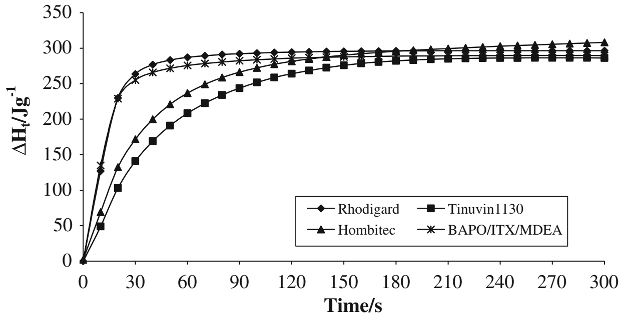


Fig. 8 Curing reaction of ebecryl 8402 + 50% HDDA initiated by BAPO/ITX/MDEA. Reaction conducted in presence of UV absorbers and under the whole light spectrum

Conversely, the UV absorbers seem to influence the reactivity of the systems by inducing some retardation and inhibition effects (Δt increases), merely for experiments carried out under monochromatic wavelengths equal or higher than 440 nm (cf. Fig. 7). UV absorbers can not be classified following their inhibition ability. Nevertheless it is noteworthy that the photoinitiators used are efficient at the different wavelengths studied whatever the UV absorber present.

By irradiating with all the wavelengths or only with the visible part of the light spectrum, the effects of UV absorbers onto the curing reaction are negligible as it can be seen on Fig. 8 since the curves showing the variation of the partial enthalpy as a function of time reach the same final value of ΔH_t.

Conclusion

The curing reaction of photosensitive systems which contain particular UV–visible photoinitiators and are therefore able to cure under daylight was investigated in presence of UV absorbers by means of photocalorimetry. We aimed to check that these compounds do not interact with the specific initiators used and inhibit the curing reaction. We could observe that UV absorbers have a great influence when oligomers are irradiated by UV wavelength by decreasing drastically the degree of cure of the resin and increasing inhibition and retardation processes. But as soon as experiments are carried out under visible light or monochromatic wavelength above 400 nm, the presence of UV absorbers in the formulations does not seem to preclude the curing reaction anymore. These results are very promising from an applied point of view insofar as such resins can be restored directly on site under sunlight and we can suppose that they could be protected by UV absorbers during their service life. So the durability of these finishing systems has now to be studied by implementing some natural or artificial ageing tests to confirm this assumption.

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