On the Inhibiting Effect of Phenolic Compounds in the Photopolymerization of Acrylates Under High-Intensity and Polychromatic UV/Visible Lights

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ABSTRACT: The photopolymerization of wood coatings under UV and visible light in industrial type conditions has been investigated. The inhibiting effect of the phenolic compounds found in wood extractives, especially quercetin, on the final properties of the coating (hardness, gel content) as well as the polymerization kinetics (rates, final conversion) has been discussed. Model clear-coating formulations — based on an acrylate oligomer, a reactive diluent and a bis-acylphosphine oxide as photo-initiator — have been used. This article focuses on the influence of the nature of the acrylate oligomer (polyester, epoxy, polyurethane), the type of phenolic derivative (POHs) and the irradiation conditions (UV conveyor, Xe lamp). It appears that lead to through the strong inner-filter effect in the presence of quercetin is responsible for the loss of all the observed properties. In order to mimic what happens at the wood–coating interface, the role of the diffusion of the phenolic derivatives have been also investigated and discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3285–3298, 2007

Key words: photopolymerization; photo-initiator; phenol; wood coating

INTRODUCTION

Wood coating is an important field of applications in the Radiation Curing technology (see, for example, Fouassier[1]). Experimental observations made in the furniture industry show that the curing of radical formulations usable as varnishes on wood species suffer from inhibition effects (which result in lower rates of polymerization and longer inhibition times at the beginning of the reaction). These effects are more or less marked and depend on the wood substrate (the effect is important with exotic woods), the nature of the oligomer matrix, and the photo-initiating system (PIS). The inhibiting effects are attributed to the wood extractive components[2a] — especially phenolic derivatives (POHs) whose effects are known in thermal polymerization reactions[2b] — migrating from the wood–coating interface into the resin. The role of phenolic compounds on the cure extent during the curing process and their effect on the properties of the coating do not seem to have been studied in detail. In a previous work,[3] the inhibiting effect of these derivatives on the photopolymerization of acrylate formulations was focused on the effect of a selected POHs on the initiating step and the kinetics of the polymerization. This study was made in model irradiation conditions, i.e., in laminate, under low intensity with monochromatic or filtered lights in order to selectively excite the photo-initiator.

This article is devoted to the study in industrial type conditions (high light intensity, polychromatic light, and under air). The inhibiting effects of a large set of model phenolic derivatives, representative of the wood extractives, on the final properties of a photopolymerized coating (such as hardness, gel content, or conversion degree) as well as the polymerization kinetics are evaluated. The selected photo-initiator used in these experiments is a bis-acylphosphine oxide derivative BPO; several commercial mixtures containing this compound are recommended in the wood-coating applications. The effect of the POHs migration from a substrate into the resin — which mimic what happens at the wood–coating interface in real conditions — will also be investigated. The results will allow a general discussion of this inhibition effect which are of prime importance in the wood-coating industry.

EXPERIMENTAL

Materials

Compounds

Formulations based on an acrylate oligomer, a reactive diluent and a photo-initiating system were used

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as model clear coatings. Five acrylate oligomers with different backbones were selected: a polyester diacrylate Ebecryl® 81 (PE), two epoxy diacrylates Ebecryl® 605 and Ebecryl® 3500 (POE1 and POE2), an aliphatic polyurethane triacrylate Ebecryl® 264 (PU1) and an aliphatic polyurethane diacrylate Ebecryl® 284 (PU2), all from Cytec Chemicals. 1,6-Hexanediol diacrylate (HDDA) from Cytec Chemicals was used as a reactive diluent (50/50 w/w %). A complex formulation (FLab), designed elsewhere[3] and based on 25% polyethyleneglycol (400) diacrylate Sartomer® 344 (SR 344) from Cray Valley (Verneuil en Halatte, France), 10% isobornyl acrylate Sartomer® 506* (SR 506) also from Cray Valley, 25% aliphatic polyurethane diacrylate Actilane® 200 from Akzo Nobel (Arnhem, Netherlands), and 10% HDDA from Cytec Chemicals (Brussels, Belgium), was also used.

Phenyl-bis-(2,4,6-trimethylbenzoyl) phosphine oxide, Irgacure 819 (BPO) from Cray Valley, purchased from Ciba Specialty Chemicals, was used as the photo-initiator.

The formulations were applied on glass plates or BaF_2 crystal windows with a calibrated wire-wound bar, as a uniform film of 25 or 100 μm thickness, depending on the analytical method applied to the sample.

Phenolic derivatives

Various POHs compounds were directly added into the bulk formulations (1% w/w). The selected mono- and polyphenolic compounds are divided into four classes, depending on their chemical structure: i) ethylenic monophenols — trans-4-hydroxystilbene, coniferaldehyde (4-hydroxy-3-methoxycinnamaldehyde), sinapic acid (4-hydroxy-3,5-dimethoxycinnamic acid); ii) non-ethylenic monophenols — vanillin (4-hydroxy-3-methoxybenzaldehyde); iii) polyphenols with flavonoids — morin (2′,3,4′,5,7-pentahydroxyflavone), quercetin (3,3′,4′,5,7-pentahydroxyflavone), catechin (3,3′,4′,5,7-pentahydroxyflavane), and flavone as a parent compound; and iv) tannin models (ellagic acid: (2,3,7,8-tetrahydroxy 1 benzopyrano 5,4,3, benzopyran-5,10-dione)) and gallic acid (3,4,5-trihydroxybenzoic acid). In the case of quercetin for example, these experiments will be further referred as ''quercetin in bulk'' (Q_{bulk}) experiments.

However, by adding phenolic derivatives into the formulations, is not very representative of what really happens when the film is directly applied on a wood sample. In order to mimic the phenomena occurring at the wood–coating interface, a specific operating mode has been developed. The same weighted amount of quercetin as in the Q_{bulk} experiments (1%) is laid on a glass plate by solvent evaporation. Then, the POHs free curable formulation is applied onto the deposited quercetin. The film is finally crosslinked under the UV conveyor at several times after application of the resin (called hereafter diffusion times t). These experiments will be further referred as ''quercetin at the interface'' or ''$Q_{interface}$'' experiments.

Irradiation

The photopolymerization of the coatings under visible light was performed under a 200 W Xe lamp; the light intensity was ranging from 21 mW/cm^2 to 110 mW/cm^2 in the UVA-UVB spectral range (Lightingcure L8333 apparatus equipped with an L8253 Xe lamp from HAMAMATSU). On the other hand, experiments were also carried out using a UV conveyor (Minicure 2098 from Primarc Limited) equipped with a mercury lamp (80 W/cm), at various belt speeds leading to light doses from 90 mJ/cm^2/pass up to 1300 mJ/cm^2/pass (measured in the 320–400 nm range). All curing experiments were performed under air. Emission spectra of the light sources as well as the absorption spectra of BPO and the POHs are shown in Figure 1.

Analysis

Persoz hardness

Persoz hardness was measured after five or ten passes under the UV conveyor (depending on the conveyor belt speed) on 100 μm-thick films, using an apparatus from Braive Instruments. The error bar is ±5%.

Gel content

Films (100 μm thick) were removed from the glass plates after irradiation, weighted and swelled in acetone during 48 h and finally dried in an oven at 60°C until constant weight. The gel content was then calculated.

RT-FTIR Spectroscopy

The polymerization of the acrylate resin was followed by real-time FTIR (RT-FTIR) spectroscopy by monitoring the disappearance of the 810 cm^{-1} band of the acrylate double bond (=CH_2 twist) using the Avatar 360 from Nicolet. The % conversion was then calculated as a function of the irradiation time and the maximum polymerization rates R_p deduced from the slope of the curve in its linear part. The error bar on R_p is ±5%. The error on the final % conversion χ is generally better than ±3 for $\chi > 60\%$.

UV/Visible Spectroscopy

The UV/visible spectra of the photo-initiator and the phenolic derivatives were recorded using the Beckman DU 640. The photolysis of the photo-initiator was also followed as a function of the irradiation time.

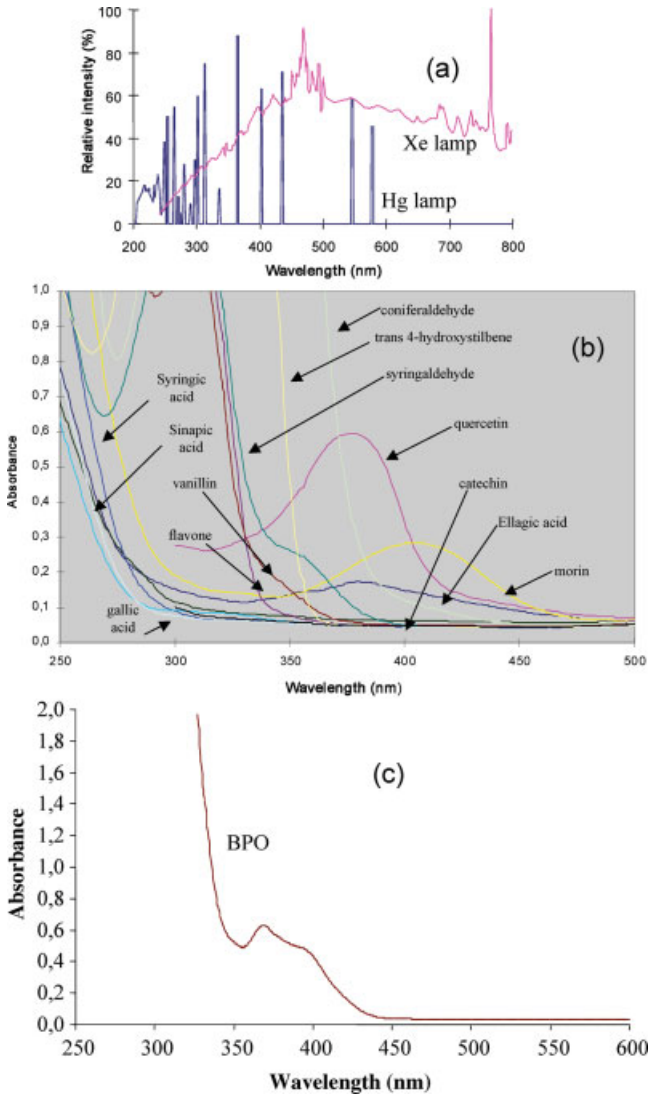


Figure 1 (a) Emission spectra of the light sources used; (b) absorption spectra of the phenolic derivatives used (at 1% in the 25 μm PU1/HDDA film). POHs very often have high extinction coefficients in the near UV/visible range, e.g., 3500 and 27000 M^{-1} cm^{-1} for coniferaldehyde and quercetin at 365 nm. These values are usually higher than those of most of the commercially available photo-initiators; (c) absorption spectrum of BPO inacetonitrile. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Definition of normalized parameters

The oligomer matrix also has a strong influence on the whole properties of the coating. In order to overcome this additional dependence, normalized parameters x_{POHs}/x_0 (where x_0 and x_{POHs} represent the studied properties measured in the absence and in the presence of phenolic derivative, respectively) will be used: the more pronounced the inhibiting effect, the lower the normalized parameter. The studied normalized properties will either be related to the Persoz Hardness H, the gel content G, the conversion degree χ, or the polymerization rate R_p. The error bar on the normalized parameters is estimated to ±5%.

RESULTS AND DISCUSSION

The role of a phenol

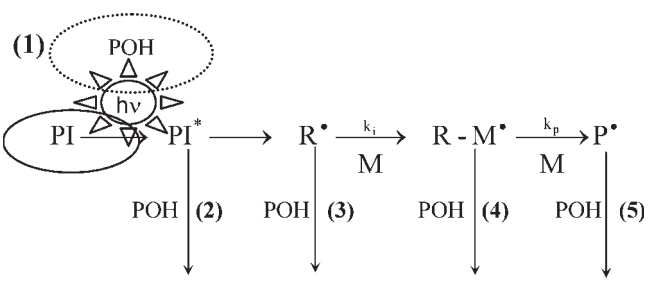
The phenolic derivatives can interact with the active species present in the medium at each step of the photoinduced polymerization reaction (Scheme 1) according to four possible effects. In the first effect, the POHs play a role through a physical phenomenon well known in photochemistry: the so-called inner-filter effect corresponds to a detrimental absorption of a fraction of the light usable by the photo-initiator (route 1). This phenomenon will obviously depend on the respective UV/visible absorption spectra of the phenolic derivatives and the photo-initiator *PI* (Fig. 1). The second effect[3] is related to the quenching of the photo-initiator excited states *PI** by the POHs (route 2) by energy transfer, hydrogen abstraction, proton, and electron transfer. The third effect[3] is an interaction with the generated initiating radicals (route 3). The last effect[2b] (routes 4 to 5) corresponds to chemical interactions (quenching of the growing chains $R–M^{\bullet}$ and $P^{\bullet}$): this effect is independent of the initiation mode and is also encountered in thermal polymerization. Moreover, phenoxyl radicals — known as efficient termination agents — are formed by such routes.

The inner-filter effect of the POHs

From the respective UV/visible absorption spectra of POHs and BPO [Fig. 1(b)], the inner-filter effect induced by the different compounds can be quantified (Table I). From the Xe lamp emission spectrum and the UV/visible absorption spectrum of a substance X, the light intensity absorbed at each wavelength $\mathbf{I}^{\lambda}_{abs}(X)$ can be calculated from the following formula:

$$\mathbf{I}^{\lambda}_{abs}(X) = N^{*}_{\lambda}(1 - 10^{-A_{\lambda}(X)})$$

where $A_{\lambda}(X)$ represents the absorbance of X at wavelength λ and N_{λ} the amount of photons emitted per sec-



Scheme 1 Interaction possibilities (routes 1 to 5) between the phenolic derivatives POHs and the photo-initiator PI and the radicals in a photo-induced radical polymerization process.

TABLE I
Fraction *F* of the Light Absorbed by the Photo-Initiator[a]

POHs	$F = \Sigma\ \mathrm{Iabs}_{\mathrm{BPO}}(\lambda) / \Sigma\ \mathrm{Iabs}_{\mathrm{BPO+POHs}}(\lambda)$
Trans-4-hydroxystilbene	44%
Coniferaldehyde	35%
Sinapic acid	78%
Vanillin	47%
Gallic acid	82%
Flavone	59%
Quercetin	18%
Catechin	77%
Ellagic acid	56%

[a] Calculation of the inner filter effect (parameter *F*: see text) induced by 1% of POHs (0.5% if Favone) into a formulation containing 2% of BPO. Light source: Xe Lamp.

ond and square centimeter at wavelength λ by the Xe lamp. N_λ can be itself determined from the Xe lamp emission spectrum. The total intensity (P_0) of the light emitted by the Xe lamp over the whole emission spectrum is thus linked to I_λ (the intensity of the Xe lamp at wavelength λ) by the following equation:

$$P_0 = \sum_\lambda I_\lambda = \sum_\lambda k * I_\lambda^{\mathrm{rel}}$$

where $\boldsymbol{I}_\lambda^{\mathrm{rel}}$ is the relative intensity of the Xe lamp at wavelength λ and *k* is a proportionality factor deduced from the P_0 measurement and the relative emission spectrum [Fig. 1(a)]. Finally, N_λ is equal to

$$N_\lambda = \frac{I_\lambda}{\frac{hc}{\lambda} * N_A}$$

where *h* is the Planck's constant, *c* the light speed, and N_A is the Avogadro number. The light intensity absorbed at each wavelength by the photo-initiator and the phenolic derivative, $\mathbf{I}_{\mathrm{abs}}^{\lambda}$(Irg 819) and $\mathbf{I}_{\mathrm{abs}}^{\lambda}$(POHs), respectively, was then calculated; the inner-filter effect was evaluated for each phenolic derivative through parameter *F*, defined as the ratio between the amount of light absorbed by the photo-initiator and the total amount of light absorbed by the whole formulation (PI + POHs):

$$F = \frac{\sum_\lambda \mathbf{I}_{\mathrm{abs}}^{\lambda}(\mathrm{Irg\ 819})}{\sum_\lambda \mathbf{I}_{\mathrm{abs}}^{\lambda}(\mathrm{Irg\ 819}) + \sum_\lambda \mathbf{I}_{\mathrm{abs}}^{\lambda}(\mathrm{POHs})}$$

All POHs (see Table II) lead to a noticeable inner-filter effect ($F \leq 80\%$). The most pronounced inner-filter effect is observed for quercetin as the photo-initiator only absorbs 24% of the total amount of light. The lowest inner-filter effects (corresponding to $78 < F < 82\%$) were obtained in the presence of mono-aromatic phenolic derivatives like the sinapic acid and the gallic acid. A first classification of the phenolic derivatives as a function of their *F* factor was thus established (route 1).

Evaluation of the POHs reactivity towards radicals

A large number of publications have been devoted to the evaluation of the antioxidant activity and/or anti-radical activity of POHs, especially flavonoids.[4–8] They can also be used in order to predict the possible interactions of the POHs with the free radicals present in the medium (routes 3 to 5). A common scale of antioxidant activity, the Trolox Equivalent Antioxidant Activity (TEAC) value, is based on the substance capacity to scavenge the 2,2′-azinobis-(3-ethylbenzothiazoline-6-

TABLE II
Antioxidant and Antiradical Properties of the Studied Compounds

	Antioxidant activity	Antiradical activity		
			k_{app} (s^{-1}) = k_{real}[a] (extractive) [8]	
Extractive	TEAC (mM)[a]	EC_{50} [7]	[Extractive] (mol L^{-1})	k_{app} (s^{-1})
Ellagic acid	—	0.10	10^{-3}	0.24
Quercetin	(a) 4.72 ± 0.10; (b) 4.84 ± 0.45; (c) 4.7	0.14	10^{-3}	2.10
			10^{-2}	4.53
Morin	(a) 2.55 ± 0.02; (b) 2.60 ± 0.24	0.25	10^{-3}	3.48
			10^{-2}	18.3
Catechin	(a) 2.40 ± 0.05; (b) 3.42 ± 0.43; (c) 2.4; (d) 2.28 ± 0.04	0.13	10^{-2}	1.44
Flavone	(b) 0.30 ± 0.10	—	—	—
Gallic acid	(a) 3.01 ± 0.05; (b) 2.69 ± 0.41	0.15	10^{-2}	0.35
Vanillic acid	(a) 1.43 ± 0.05; (d) 0.67 ± 0.09	1.00		
Vanillin	(d) 0.13 ± 0.01	—	—	—
Sinapic acid	—	0.30	10^{-2}	0.81
Trans-4-hydroxystilbene	—	—	10^{-2}	0.7

[a] TEAC values reported in refereneces (see text): (a) ref. [5]; (b) ref. [1]; (c) ref. [6]; (d) ref. [4]. For ferulic acid which corresponds to coniferaldehyde, the values are: TEAC = 1.9 ± 0.02,[1] EC_{50} = 0.44.[7] These values are considered the upper values for coniferaldehyde.

TABLE III
Influence of the Phenolic Derivatives on the Hardness of POE1 Films Containing 2% BPO and 1% POHs (or 0.5% if flavone); Determination of the Normalized Parameter H_{POHs}/H_0.

Phenolic derivative (Abbreviation)	H_{POHs}/H_0 After 5 passes 475 mJ/cm^2	H_{POHs}/H_0 After 10 passes 950 mJ/cm^2
Without POHs	100%	100%
Trans-4-hydroxystilbene	94%	109%
Sinapic acid	92%	101%
Vanillin	101%	108%
Gallic acid	100%	105%
Flavone	106%	105%
Catechin	95%	102%
Ellagic acid	87%	101%
Coniferaldehyde	66%	71%
Quercetin	35%	40%

sulfonate) cation radical $ABTS^{\bullet+}$ compared with a standard (the Trolox: a water soluble vitamine E analog).[4] The TEAC is quantified by the Trolox solution concentration having the same antioxidant activity than a 1 mM studied compound solution: the higher the TEAC value, the higher the antioxidant activity.[5,6] On the other hand, the antiradical activity is evaluating by measuring the substance capacity to scavenge the 1,1-diphenyl-2-picrylhydrazyl free radical $DPPH^{\bullet}$.[7] This radical neither reacts with oxygen nor with itself, but very rapidly disappears in the presence of substances bearing abstractable hydrogens, which leads in the case of phenolic derivatives to the formation of phenoxyl radicals.[8] The antiradical activity may thus be measured through the EC_{50} parameter, defined as the ratio between the antioxidant concentration necessary to reduce the $DPPH^{\bullet}$ initial concentration and the $DPPH^{\bullet}$ initial concentration.[7] Another parameter based

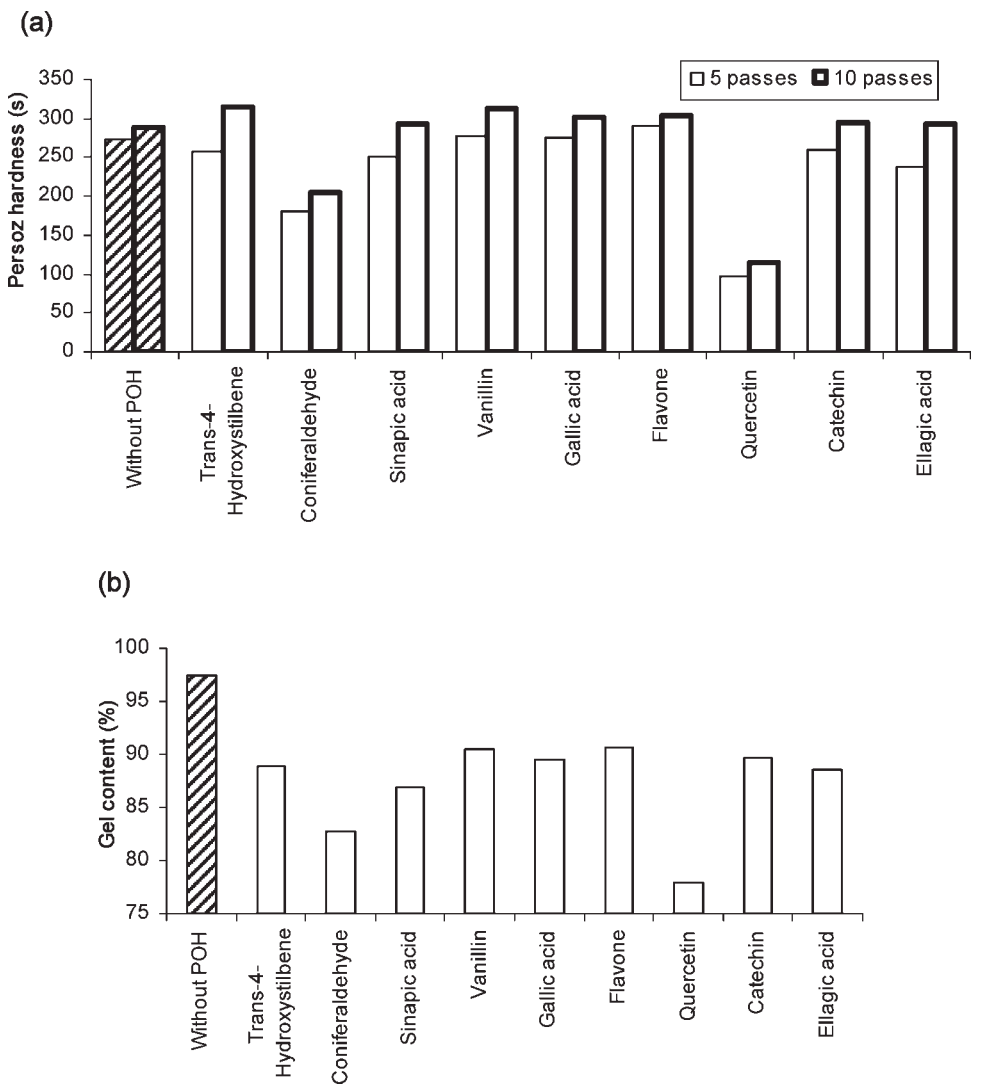


Figure 2 Influence of the phenolic derivatives on film hardness and gel content. Eb605 + 2% BPO + 1% POHs (0.5% flavone). Measurements are made on 100 μm-films after irradiation under the UV conveyor (v = 52.6 m/mn, P = 80%, I_0 = 95 mJ/cm^2/pass): (a) hardness measurements after five and ten passes under the UV conveyor; (b) gel content measurements after 10 passes under the UV conveyor.

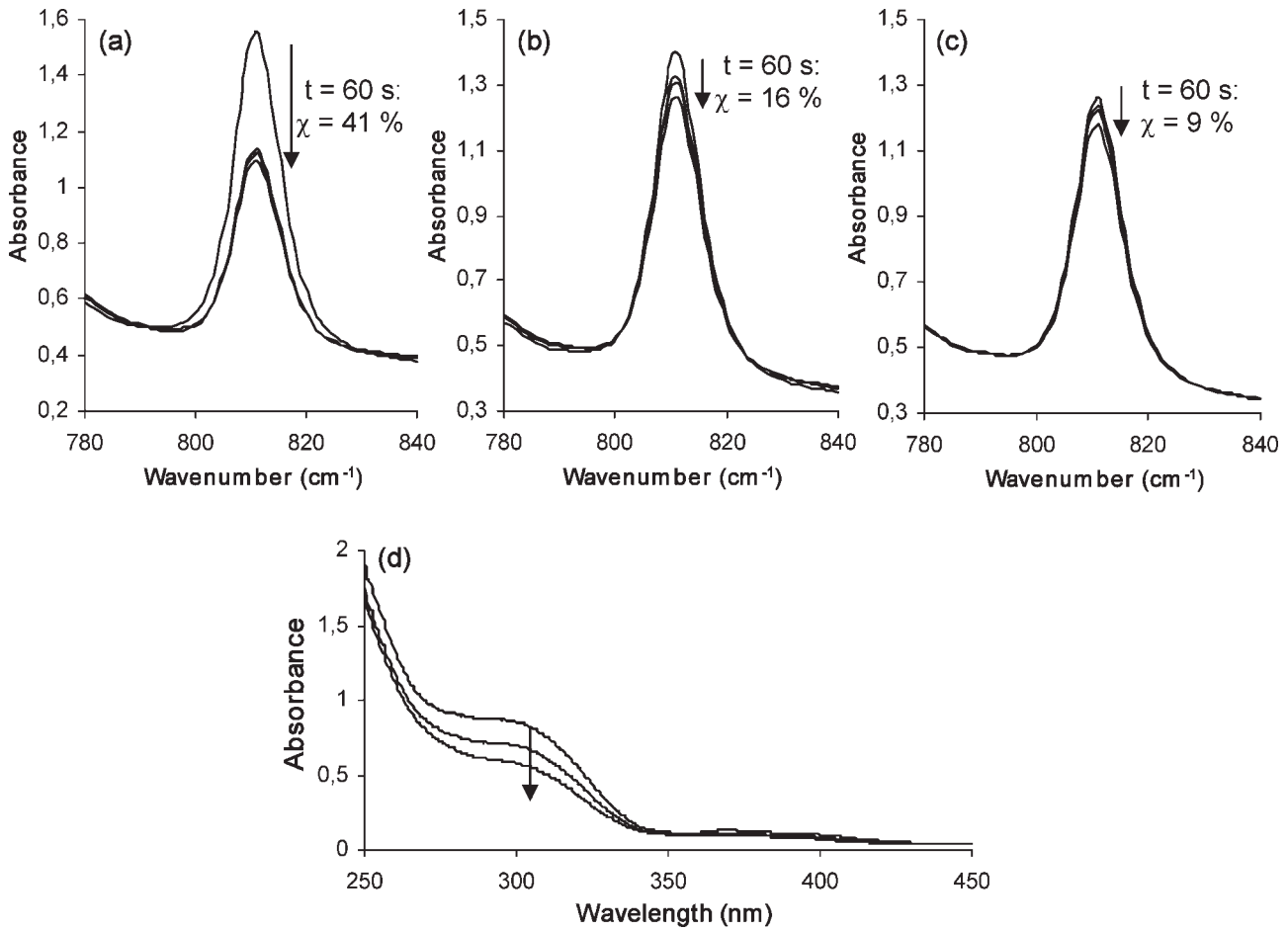


Figure 3 Evolution of the IR absorption band at 810 cm^{-1} of the PU1/HDDA + 2% BPO formulation (25 μm) as a function of the irradiation time under the Xe lamp (t = 0, 10, 20, and 60 s) in the following experimental conditions: (a) without coniferaldehyde; (b) + 1% coniferaldehyde; and (c) with external filter. (d) BPO photolysis as a function of the irradiation time (t = 0, 20 and 60 s) in a PU1/HDDA + 2% BPO″ formulation (25 μm) with external filter and Xe lamp.

on the apparent rate of the addition reaction of the phenol to the $DPPH^{\bullet}$ radical can also be used to quantify the antiradical activity.[8] These parameters concerning all the studied substances are summarized in Table II. From Tables I and II, the following classifications of the phenolic derivatives can also be compiled, depending on their inner-filter effect and antioxidant properties: quercetin is both an high light absorbing and antioxidant species, whereas coniferaldehyde should mainly present an inner-filter effect during the curing process.

Influence of the nature of the phenolic derivatives

Effects of the phenols on hardness and gel content

The Persoz hardness was measured on samples crosslinked under the UV conveyor irradiation under air. In standard irradiation conditions (v = 4.5 m/mn, I_0 = 1430 mJ/cm^2/pass), complete crosslinking occurs after only one or two passes, even in the presence of POHs. In order to boost the inhibiting effects, experiments were performed at lower light doses and high belt speed (v = 52.6 m/mn, I_0 = 95 mJ/cm^2/pass). Considering the hardness measured after five or ten passes under the UV conveyor (Table III and Figure 2(a), only quercetin and coniferaldehyde have a noticeable influence on the film hardness (strong decrease). The effect of the other derivatives — already weak after only five passes — completely disappears when increasing the number of passes under the conveyor (i.e., the total irradiation time).

The gel content was determined for the same samples after 10 passes under the UV conveyor [Fig. 2(b)]. Whereas the film hardness is only weakly affected by addition of most of the POHs (except quercetin or coniferaldehyde), the gel content decreases in all cases. The lowest gel contents are observed in the presence of coniferaldehyde and even more so in the presence of quercetin.

It can be stated that the POHs effect is not simply connected with the chemical structure of the compound. There is no correlation between, e.g., the gel content and the antioxidant activity or the increase of the inner-filter effect. For example, coniferaldehyde and gallic acid are two mono-aromatic com-

pounds. As mentioned above, coniferaldehyde presents a high inner-filter effect and low antioxidant activity, whereas gallic acid has a low inner-filter effect and a high antioxidant activity; this means that coniferaldehyde behaves as a light absorber and gallic acid mostly acts as a radical scavenger. On the other hand, quercetin and catechin — 2 poly-aromatic compounds — have both a high antioxidant activity and a high antioxidant activity against a low inner-filter effect, respectively, which suggests that the two routes (inner-filter effect and radical scavenging) are present with quercetin, whereas catechin should only play the role of a radical scavenger.

The influence of the POHs in routes 4 and 5 — which cannot be evaluated in the present experiments — contributes to some extent to the overall inhibition effect (as exhibited in the AIBN thermally initiated polymerization of a triacrylate).[3d]

The most pronounced effects are observed in the presence of quercetin (as was observed in model irradiation conditions with a 365 nm monochromatic light and in laminate).[3] The experiments show that only coniferaldehyde and quercetin lead to a noticeable decrease of the final properties of the coatings (gel content, hardness), which is in line with a loss of the amount of light available for the excitation of the photo-initiator.

The effect of a POHs on the photo-initiator excited state itself can be ruled out. In fact, the triplet-state lifetime of BPO is too short to allow quenching. It has already been shown that the initiating radicals generated by BPO are not significantly quenched by the POHs.[3c] Routes 2 and 3 in Scheme 1 can thus be neglected. Such a behavior is usual in efficient cleavable photo-initiators.[3d]

The main role of the inner-filter effect was confirmed by the following experiment. The polymerization kinetics of the formulation was followed by RT-FTIR spectroscopy in the three following experimental conditions: (a) in the absence of coniferaldehyde; (b) in the presence of coniferaldehyde; (c) in the absence of coniferaldehyde in the formulation, but by introducing in the experimental setup an external filter which reproduces the coniferaldehyde absorption (a quartz cell containing a solution of coniferaldehyde in methanol at such concentration that the UV/visible absorptions of coniferaldehyde measured in the liquid cell and in the 25 μm-thick PU1/HDDA film are the same). The polymerization reaction [Fig. 3(b,c)] is similarly affected (slightly more when the external filter is added): the main action mode of this phenol actually originates from an inner-filter effect lowering the polymerization rate by decreasing the BPO decomposition rate. It can thus be concluded that the observed inhibition effects in a phoinitiated polymerization predominately originate from an inner-filter effect induced by the mono- as well as the poly-aromatic phenolic derivatives.

Influence of the POHs and quercetin concentration

In practical conditions using wood substrates, it is difficult to evaluate the amount of phenolic derivative which will migrate into the resin after the film application before and during irradiation, i.e., before and during polymerization. In the case of an oak wood rich in colored extractives (from 8 to 12 % of the dry wood mass), the extractive content will vary from 50 to 90 mg/cm^3 (for an oak wood having a density between 0.7 and 0.85). In our mixtures, the phenolic derivatives are introduced at 1 w % into the formulations, which corresponds to 10 mg/cm^3 for quercetin. For a 100 μm-thick film applied on 1 cm^2 surface of a wood sample, the resin should penetrate up to 11 or 20 μm into the wood structure to reach such an extractive concentration. Ellagic acid and vescalagin contents can reach 1.5 mg/g of dry material, which corresponds to 1.1 mg/cm^3 and 17 mg/g of dry material (13 mg/cm^3 of wood), respectively.[8] Exotic wood species are far more

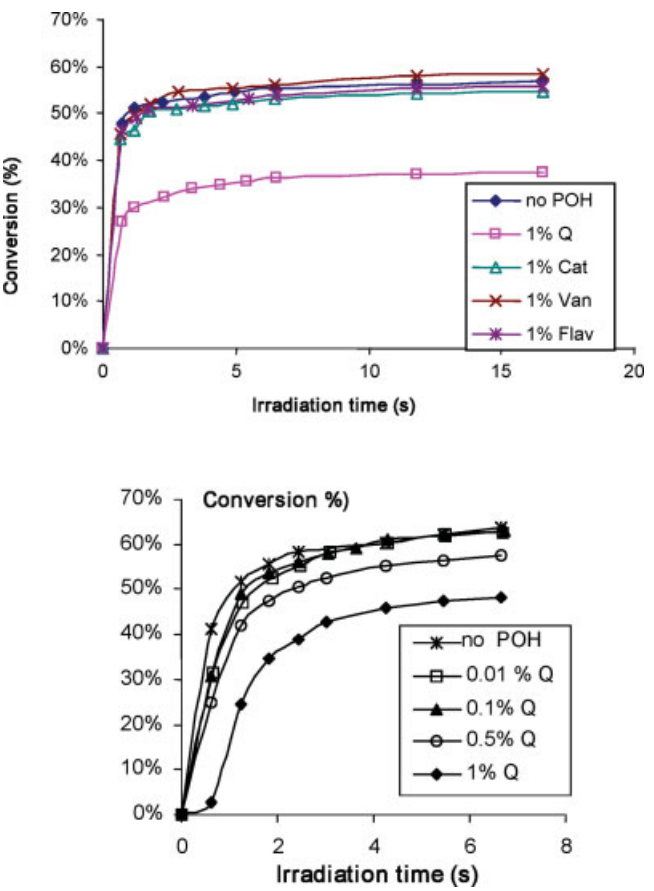


Figure 4 Top: influence of the POHs on the polymerization kinetics of PE + 2% BPO + 1% POHs formulations (15 μm). Xe lamp. P_0 = 50 mW/cm^2. Bottom: influence of the quercetin concentration on the polymerization kinetics of FLab + 2% BPO + x% Q formulations (15 μm). Xe lamp. P_0 = 21 mW/cm^2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

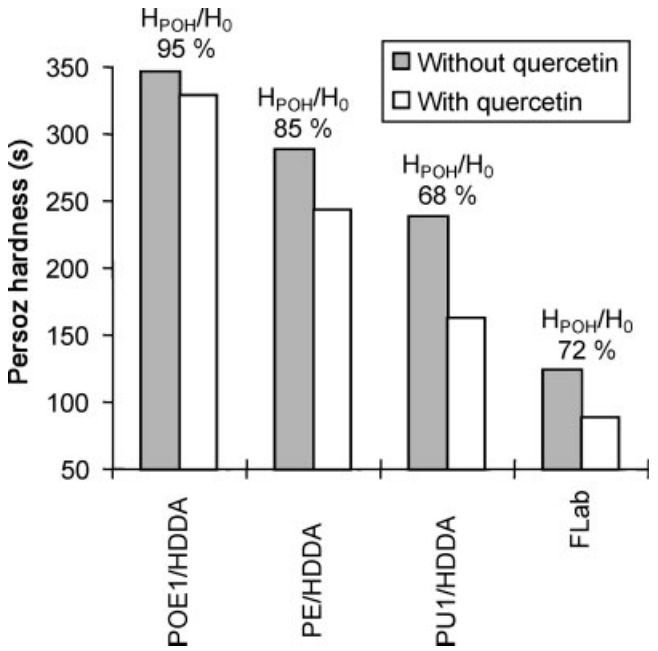


Figure 5 Effect of quercetin (1%) on the film hardness measured after five passes under the UV conveyor ($v = 4.5$ m/mn, $I_0 = 1430$ mJ/cm^2/pass) as a function of the oligomer structure. Determination of the normalized parameter H_{POHs}/H_0.

charged in extractives. This is the reason why the phenolic derivatives have to be introduced at a sufficient high concentration.

Figure 4 shows the influence of the nature of three representative phenolic derivatives (quercetine, vanillin, and catechin) and flavone on the polymerization kinetics and the concentration effect when using quercetine. Only quercetine leads to a significant effect on the polymerization rate and the final conversion degree. The quercetin concentration was changed from 0.01% to 1% in order to observe the concentration effect on the induced inhibition phenomena: the rate of polymerization as well as the maximum % conversion decrease. At high light intensity, some effect is only detectable on the film hardness (Fig. 5, Table IV) at high quercetin concentration (1%). At low light intensity (Fig. 4), the polymerization rate decreases even at very low concentrations (0.01 and 0.1%), whereas the final conversion degree is only affected for a quercetin concentration above 0.5%. At a wood–coating interface, quercetin should lead to strong effects even if the concentration remains low in the upper domain.

Influence of the light dose

The Persoz hardness of POE1/HDDA cured formulations containing quercetin was also measured at different belt speeds in order to study the influence of the light intensity or the light dose. This system — weakly sensitive to the presence of quercetin when receiving a sufficiently high light dose — was shown to be strongly affected at low intensity irradiation (Table V).

Influence of the multifonctional oligomer structure

The inhibiting effects induced by the POHs was also studied as a function of the oligomer chemical structure: epoxy acrylate (POE1 and POE2), polyester acrylate (PE) and polyurethane acrylate (PU1, PU2, and FLab). As seen in Figure 6 and Table VI (UV conveyor, high dose), the effect induced by quercetin on the hardness and gel content effectively seems to be a function of the type of the matrix. The polyester acrylate-based resins and, even more so, the epoxy-acrylate based resins are only weakly affected by the presence of quercetin, contrary to urethane acrylate-based resins.

The effect of quercetin on the hardness of the different resin-based films (Table VII) strongly depends on the light intensity. The epoxy acrylate-based resins are strongly sensitive to the addition of quercetin at low light dose which leads to a decrease of the hardness and gel content as large as for polyurethane acrylate-based formulations. If considering

TABLE IV
Influence of the Quercetin Concentration on Polymerization Kinetics (R_p and γ) and Hardness[a]

	Xe lamp: $P = 100\%$, $P_0 = 100$ mW/cm^2		Xe lamp: $P = 20\%$, $P_0 = 21$ mW/cm^2		UV conveyor $I_0 = 1430$ mJ/cm^2/pass
[Q]	$R_{p}POHs/R_{p0}$	χ_{POHs}/χ_0	$R_{p}POHs/R_{p0}$	χ_{POHs}/χ_0	H_{POHs}/H_0
0.01%	95%	100%	73%	99%	97%
0.1%	91%	98%	71%	97%	93%
0.5%	89%	97%	60%	88%	85%
1%	81%	94%	45%	76%	72%

[a] FLab films with 2% BPO and x% Q. Kinetics followed on 15 μm-thick films exposed to the Xe lamp at various light intensities. Hardness measurements made on 100 μm-thick films after five passes under the UV conveyor ($v = 4.5$ m/mn, $P = 100\%$, $I_0 = 1430$ mJ/cm^2/pass).

TABLE V
Effect of Quercetin (1%) on the Film Hardness of POE1/HDDA Cured Formulations (in the presence of 2% BPO) as a Function of the Light Dose (Belt Speed v, number of passes p)[a]

POE1/HDDA Persoz hardness (s)	Without quercetin	Q_{bulk}	H_{POHs}/H_0 Q_{bulk}
v = 4.5 m/mn, P = 100%, 5 p 7150 mJ/cm^2 in 5 p	347	329	95%
v = 24 m/mn, P = 100%, 10 p 2520 mJ/cm^2 in 10 p	348	325	93%
v = 52 m/mn, P = 80%, 15 p 1425 mJ/cm^2 in 15 p	332	Non-measurable Sticky	0%

[a] UV conveyor at different belt speeds and powers.

the hardness, the PE-based formulations remain less affected by the presence of quercetin. However, the quercetin addition leads to a gel content decrease whatever the matrix. Urethane acrylate-based matrices proved to be particularly sensitive to the quercetin inhibiting effect. But, whereas the hardness decrease of the PU2 resin was less pronounced than that of the PU1 resin, the gel content decrease is far higher. The PU2 resin is a difunctional resin, while the PU1 resin is a trifunctional one: the gel content of the latter will be thus less affected for a given conversion degree. This also explains why the PU1-based formulation — presenting a strong decrease of the film hardness in the presence of quercetin — has a relatively high gel content (higher than that of other difunctional resins such as PE).

The polymerization kinetics were also followed by RT-FTIR spectroscopy on 25 μm-thick films under the Xe lamp at different intensities (Table VII). With BPO as a photo-initiator, the quercetin addition leads to a decrease of both the polymerization rate and the final conversion degree which depends on both the matrix and the light intensity. At high light intensity (100 mW/cm^2), the decrease of the polymerization rate and of the conversion degree is not very significant and is comparable when going from an oligomer to another, with the PE polyester acrylate being less affected. At low light intensity (21 mW/cm^2), the results are found similar (Fig. 4) to those observed when working with the UV conveyor at high belt speeds: epoxy acrylate is thus very affected by the quercetin addition. The rank for the final conversion degree is comparable to that observed for the hardness: polyester acrylate PE < polyurethane acrylate PU1 < epoxy acrylate POE1. But the FLab formulation (though also a polyurethane acrylate-based mixture) is the less affected. For a given photo-initiating system, changing the oligomer results in a different efficiency for the POHs/matrix interaction reactions (routes 4 and 5 in Scheme 1).

All these data mean that, upon addition of quercetin:

- at a high energy dose (i) the polymerization rate, the final conversion degree, and the hardness remain high for a given matrix, the reactivity being very high and the detrimental effect of the POHs roughly identical from a formulation to another, and (ii) the evolution of the hardness is dependent on the matrix but the polymerization kinetics are almost similar whatever the matrix;

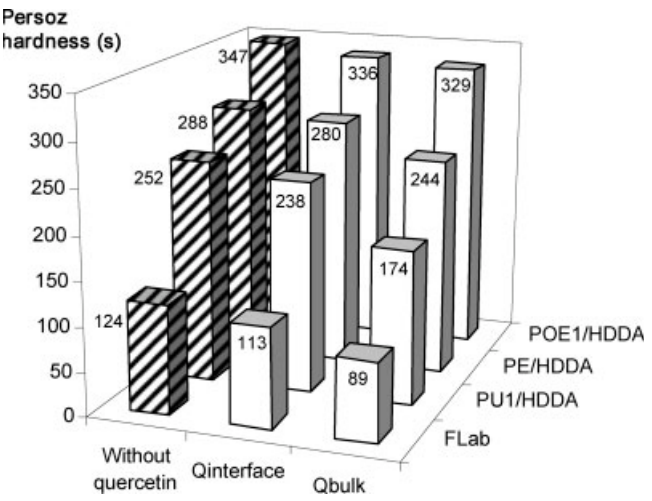


Figure 6 Effect of quercetin (1%) on the film hardness measured after five passes under the UV conveyor (v = 4.5 m/mn, I_0 = 1430 mJ/cm^2/pass) as a function of the oligomer structure. Determination of the normalized parameter H_{POHs}/H_0.

TABLE VI
Effect of Quercetin (1%) at Low Light Dose (UV Conveyor, v = 52.6 m/mn, P = 80%, I_0 = 95 mJ/cm^2/pass) on Film Hardness and Gel Content as a Function of the Chemical Structure of the Acrylate Oligomer[a]

		Normalized parameter	
Oligomer		H_{POHs}/H_0 Q_{bulk}	G_{POHs}/G_0 Q_{bulk}
Epoxy diacrylate	POE1	40%	80%
	POE2	37%	85%
Polyester diacrylate	PE	96%	78%
Polyurethane triacrylate	PU1	51%	84%
Polyurethane diacrylate	PU2	64%	62%

[a] 100 μm-thick films; 10 passes.

TABLE VII
Effect of Quercetin (1%) on Polymerization Kinetics as a Function of the Oligomer Structure[a]

	Intensity					
	100 mW/cm^2		21 mW/cm^2			
Formulation	$R_{p\text{POHs}}/R_{p0}$ Q_{bulk}	$\chi_{\text{POHs}}/\chi_0$ Q_{bulk}	$(R_p/[M]_0)_0$ (10^2 s^{-1})	χ_0 (%)	$R_{p\text{POHs}}/R_{p0}$ Q_{bulk}	$\chi_{\text{POHs}}/\chi_0$ Q_{bulk}
POE1/HDDA	86%	91%	37	44	4%	14%
PE/HDDA	87%	99%	44	62	19%	70%
PU1/HDDA	90%	93%	41	50	31%	41%
FLab	81%	94%	61	78	45%	76%

[a] Xe lamp at different light intensities (21 or 100 mW/cm^2). Determination of the normalized parameters $R_{p\text{POHs}}/R_{p0}$ and $\chi_{\text{POHs}}/\chi_0$. See text.

- at a low energy dose (i) the polymerization rate and the final conversion degree are dependent on the matrix and (ii) the hardness drops down.

Simulation of the diffusion of a phenolic compound at an interface

When the irradiation is carried out just after the application ($t < 15$ s), a slight decrease of hardness is observed (Fig. 7 and Table VIII), even for a very short diffusion time as the film is irradiated just after its application ($t \leq 15$ s). The measured hardness is intermediate between that measured in the Q_{bulk} experiments and that measured in the absence of phenolic derivative: it means that quercetin effectively diffuses into the monomer matrix. The most affected formulations are again the polyurethane acrylates (PU1/HDDA and FLab).

The kinetics of the polymerization performed at low intensity under the Xe lamp were also followed by RT-FTIR spectroscopy on 25 μm-thick films (Fig. 8 and Table IV). The $Q_{\text{interface}}$ experiments take evidence of a large inhibiting effect even if the resin is irradiated just after its application ($t \leq 15$ s), leading to polymerization rates and conversion degrees intermediate between those measured in the absence of quercetin and in Q_{bulk} experiments. The phenomenon still varies from one formulation to another. The PU1/HDDA formulation — already sensitive to the addition of quercetin in bulk — is most affected by the deposition of quercetin at the interface. Moreover, the polyester acrylate-based matrices and, even more so, the epoxy acrylate-based ones, are again less sensitive (Table IV). The other polyurethane acrylate-based formulation FLab is far less affected than the PU1-based one. Further comments are given in the next section.

If quercetin migrates into the resin, the hardness should decrease as a function of the time delay between the film application and the irradiation (diffusion time t). This assumption was checked by a $Q_{\text{interface}}$ experiment using a $t = 15$ min diffusion time. At $t = 15$ min, quercetin has migrated deeper into the formulation and the measured hardness is the same as the value measured when the same amount of quercetin was directly dissolved into the monomer mixture (Fig. 9). The Q_{bulk} experiment should then appear as the limit case of the $Q_{\text{interface}}$ experiment after complete diffusion and dissolution of the quercetin into the resin.

From the formulation viscosity, the average distance $\langle x \rangle$ on which quercetin can migrate during the

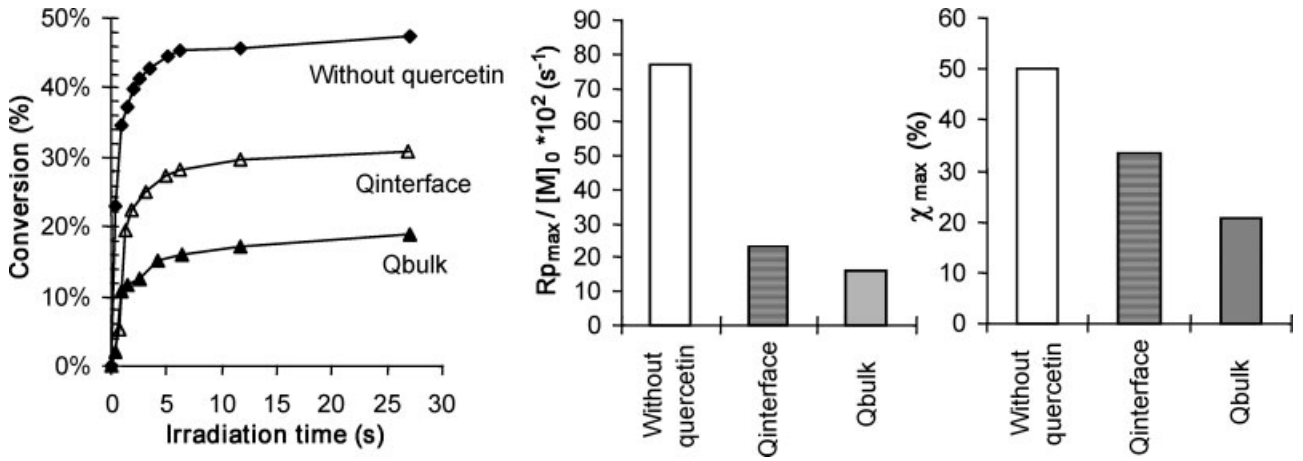


Figure 7 Polymerization kinetics as a function of the mode of introduction of quercetin. See text. PU1/HDDA + BPO 2% + Q 1%. Xe lamp. $P = 20\%$. $I_0 = 21$ mW/cm^2. 25 μm.

TABLE VIII
Effect of Quercetin Introduced in Bulk or at the Interface on Polymerization Kinetics (R_p and γ) and Film Hardness (H) as a Function of the Acrylate Oligomer Structure[a]

	UV conveyor I_0 = 1430 mJ/cm^2/pass		Xe lamp: P = 20%, P_0 = 21 mW/cm^2			
Formulation	H_{POHs}/H_0 $Q_{interface}$	H_{POHs}/H_0 Q_{bulk}	R_{pPOHs}/R_{p0} $Q_{interface}$	R_{pPOHs}/R_{p0} Q_{bulk}	χ_{POHs}/χ_0 $Q_{interface}$	χ_{POHs}/χ_0 Q_{bulk}
POE1/HDDA	97%	95%	91%	4%	84%	14%
PE/HDDA	97%	85%	37%	19%	80%	70%
PU1/HDDA	89%	68%	37%	31%	66%	41%
FLab	90%	72%	64%	45%	93%	76%

[a] 15 μm-thick films. Xe lamp (P = 20%, I_0 = 21 mW/cm^2). Hardness measurements made on 100 μm-thick films after five passes under the UV conveyor (v = 4.5 m/mn, P = 100%, I_0 = 1430 mJ/cm^2/pass). Determination of the normalized parameters H_{POHs}/H_0, R_{pPOHs}/R_{p0} and χ_{POHs}/χ_0.

diffusion time t can be estimated from the following Stokes–Einstein formula:

$$\langle x \rangle = 2\sqrt{\frac{Dt}{\pi}} \text{ and } D = \frac{k_B T}{6\pi\eta R} \text{ (Stokes–Einstein equation)}$$

where D is the diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature, η is the formulation viscosity, and R is the diffusing particle radius. The quercetin hydrodynamic radius was calculated from the molecular volume V determined by molecular modeling using a semi-empirical method (PM3): V = 281.8 Å^3 and R = 4.1 Å. The viscosities of the different formulations were measured using a Brookfield viscosimeter. The different results are summarized in Table IX.

When films are crosslinked just after their application on the quercetin layer, the quercetin has only migrated on a few μm in the depth of the formulation (from 3 to 21 μm). It is not surprising to only observe a relatively weak influence on a surface property such as hardness measured on 80–100 μm-thick films (Fig. 6 and Table IV).

However, polymerization kinetics followed on 25 μm-thick films should be strongly affected, which is experimentally observed in Figure 5 and Table IV. Considering the viscosity parameter, the POE1/HDDA and PU1/HDDA formulations should be affected in a similar way by the quercetin at the interface. The urethane acrylate-type formulations, however, proved to be much more sensitive to the quercetin addition than the epoxy ones (Fig. 5). Moreover, the quercetin action in $Q_{interface}$-type experiments also depends on the quercetin solubility in the different formulations, which is lower in epoxy acrylate-type resins. The weaker sensitivity of Flab compared to the PU1/HDDA formulation comes from its higher viscosity and its higher reactivity as well. After a 15 min diffusion time, the quercetin has migrated around 60 μm in the depth of the PU1/HDDA formulation, which explains the strong decrease in hardness as this matrix is particularly affected by the presence of quercetin.

Reduction of the inhibiting effect of the phenolic derivative

In order to balance or at least to reduce the inhibiting effect of the phenolic derivative, two parameters such as the light intensity and the photo-initiator concentration can be considered.

Influence of the light dose

As seen in Table V, the inhibiting effect of the phenolic derivative is a function of the light intensity or energy dose. The inhibiting effect, which can be negligible at low belt speed (high energy dose), depending on the oligomer matrix nature, becomes more important when increasing the belt speed (high energy dose). Considering the two matrices strongly

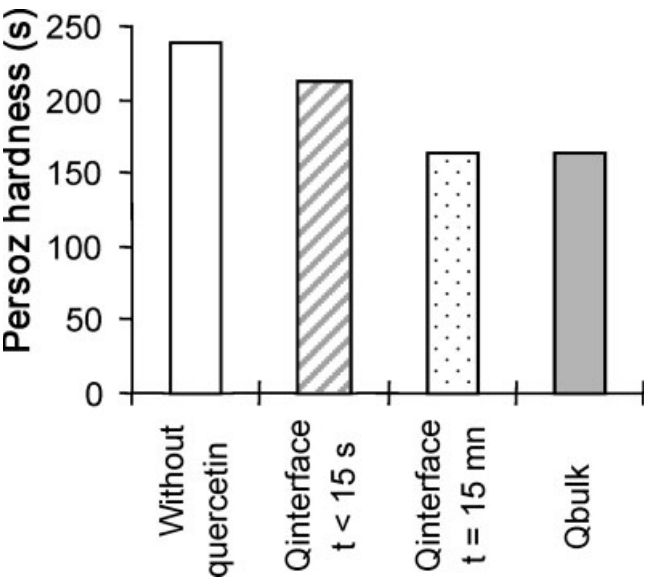


Figure 8 $Q_{interface}$ and Q_{bulk} procedure. See text. Influence of the diffusion time. Hardness measurements made after five passes under the UV conveyor (v = 4.5 m/mn, P = 100%, I_0 = 1430 mJ/cm^2/pass). Eb264/HDDA + 2% BPO + 1% Q. Thickness = 100 μm.

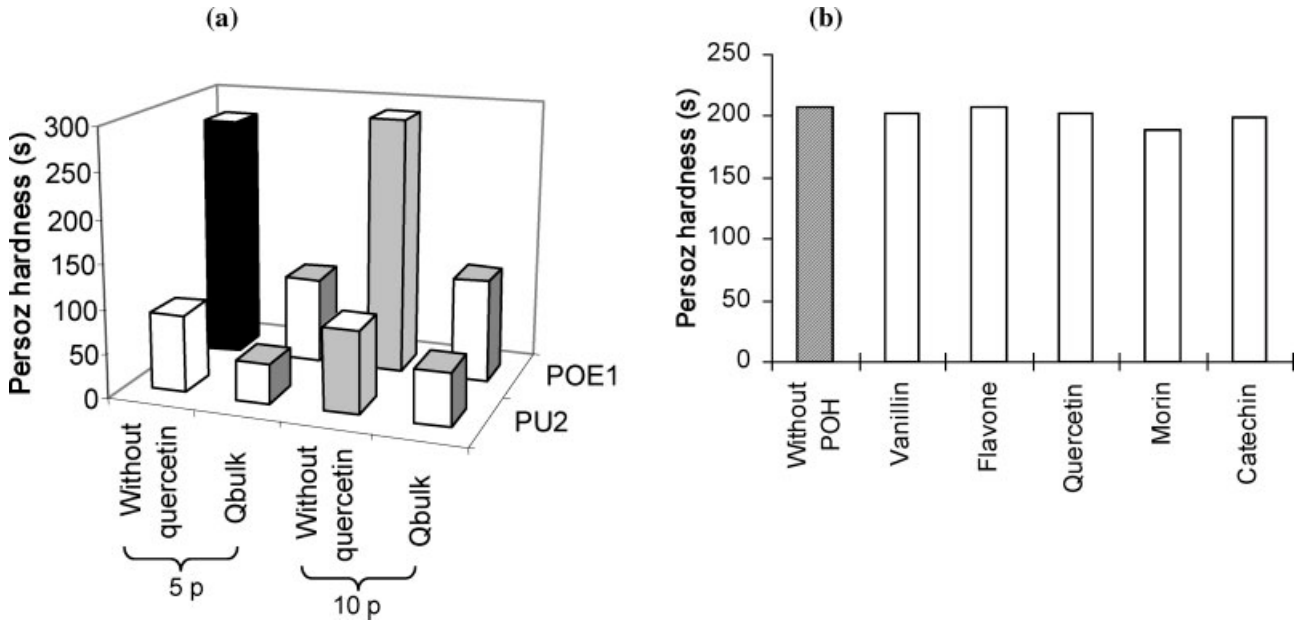


Figure 9 Influence of the diffusion time in the $Q_{interface}/Q_{bulk}$ experiments. See text. (a) Hardness measurements as a function of the number of passes under the UV conveyor (v = 52.6 m/mn, P = 80%, I_0 = 95 mJ/cm^2/pass). POE1 or PU2 + 2% BPO (+ 1% Q) formulations. (b): Hardness measurements made on PU2/HDDA + 2% BPO + 1% POHs (0.5% if flavone) formulations (100 μm) after 10 passes under the UV conveyor (v = 4.5 m/mn, I_0 = 1430 mJ/cm^2/pass).

affected by the presence of quercetin at high belt speed (POE1 and PU2, as given in Table VI), we can consider whether or not the quercetin inhibiting effect could be compensated simply by increasing the number of passes under the UV conveyor. As shown in Figure 10, the phenol inhibiting effect can be effectively reduced by increasing the light dose, but cannot be completely overcome: H_{POHs}/H_0 is equal to 36% and 40% after five and ten passes, respectively, under the UV conveyor for the epoxy matrix and 50% and 64%, respectively, for the urethane one.

As previously seen, the PU1/HDDA formulation is still affected by the presence of quercetin at v = 4.5 m/mn (I_0 = 1430 mJ/cm^2/pass), despite five passes under the UV conveyor (Fig. 5), However, increasing the number of passes from five to ten allows us to efficiently decrease the inhibiting effect of the different phenolic derivatives (even quercetin). Working at low belt speed under this lamp and increasing the irradiation time (the number of passes) provide an obvious solution, but such operating conditions are not always realistic from an industrial point of view.

Influence of the photo-initiator concentration

Another parameter is the photo-initiator concentration. The influence of this factor will be observed in a concentration range from 0.5 to 2 w/w % for BPO. The film hardness and gel content are identical whatever the concentration in the absence of phenolic derivative film. Increasing the photo-initiator concentration allows us to increase the hardnesses and the gel content, even in the presence of quercetin (Fig. 10 and Table X). However, in such irradiation conditions, even a 2% concentration of BPO is not enough to totally overcome the quercetin inhibiting effect.

The influence of the concentration was also characterized by RT-FTIR spectroscopy (irradiation under the Xe lamp, 110 mW/cm^2). The conversion degree is a function of the photo-initiator concentration, even in the absence of quercetin. The quercetin inhibiting effect is very marked at 0.5% BPO as the conversion degree is only 30% versus 50% in the absence of quercetin. However, the formulation containing 2% BPO reaches a conversion degree near 60% in the presence of quercetin versus 65% without quercetin.

TABLE IX
Quercetin Average Diffusion Distance as a Function of the Diffusion Time

Formulation	η (10^{-3} Pa s)	D (m^2/s)	$\langle x \rangle$ for t = 15 s	$\langle x \rangle$ for t = 15 mn
POE1/HDDA	121	4.43×10^{-12}	9.2 μm	71.3 μm
PE/HDDA	23	2.33×10^{-11}	21.1 μm	163.5 μm
PU1/HDDA	179	2.99×10^{-12}	7.6 μm	58.6 μm
FLab	1438	3.73×10^{-13}	2.7 μm	20.7 μm

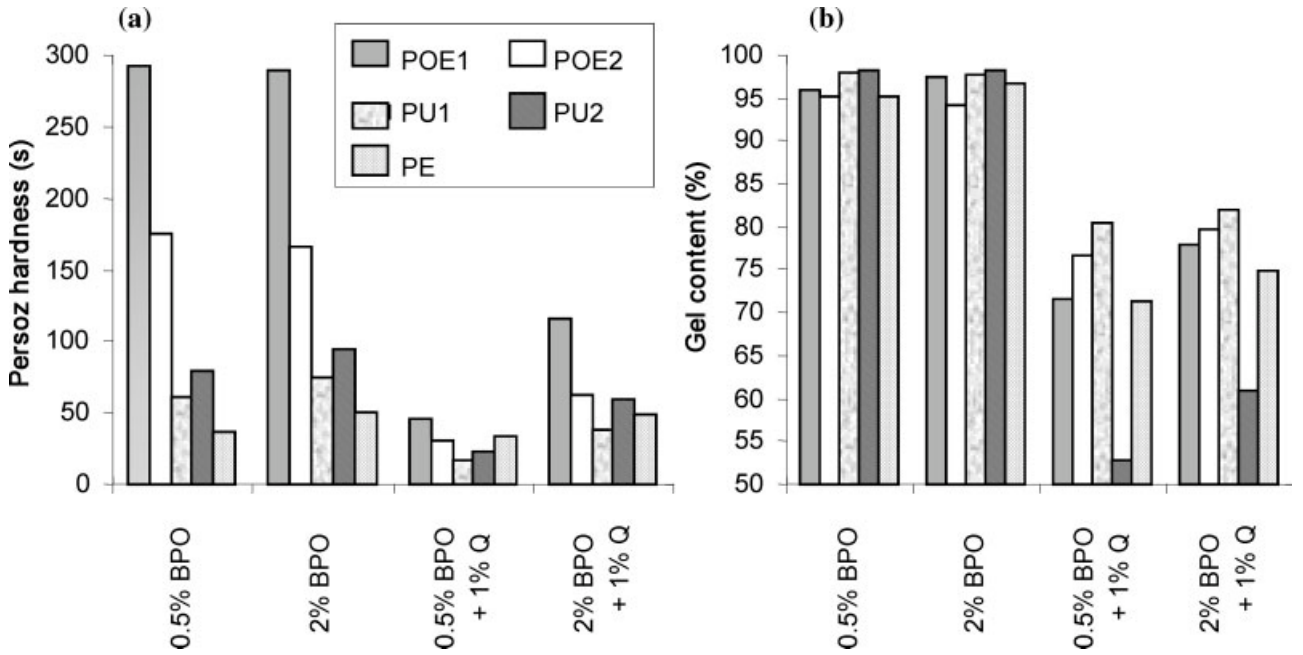


Figure 10 Quercetin effect on the film hardness and the gel content as a function of the BPO concentration and the acrylate oligomer type. Measurements made on 100 μm-thick films after 10 passes under the UV conveyor (v = 52.5 m/mn, P = 80%, I_0 = 95 mJ/cm^2/pass): (a) film hardness; (b) gel content.

CONCLUSION

The influence of wood extractives on the polymerization kinetics and the final properties of acrylate-based coatings have been studied under industrial-type conditions. From these experiments, it appears that many phenolic compounds such as coniferaldehyde and quercetin lead to a loss of the entire observed properties (polymerization rate, conversion degree, hardness, and gel content) as a result of a strong inner-filter effect. The most pronounced inhibiting effect was observed in the presence of quercetin, which corroborates the results obtained in previous studies carried out in model irradiation conditions.[3] The migration of the phenolic derivatives from wood into resin has been simulated in order to assist in the understanding of the inhibiting effects in film photopolymerization.

In the case of the photo-initiator (PI) used here, the effect of the phenolic compounds are tightly linked to the light intensity and the oligomer. At high light intensity, only the intrinsic effect on hardness due to the chemical structure is noticeable; the reactivity is generally very high and the performance loss is dependent on the matrix: the polyurethane acrylate-type resins are thus particularly affected by the quercetin addition, whereas the polyester acrylates and particularly the epoxy acrylates are only weakly sensitive. At low light intensity, not only the oligomer type but also the reactivity of each formulation have to be taken into account.

It appears that realistic control (PI concentration, light dose, wavelengths) of the detrimental inhibiting effects is rather difficult. Differences are still expected when using other PIs exhibiting a suitable absorption; a careful selection of the PIs and the light source may help to improve the results. This question will be developed in a forthcoming article.

TABLE X
Influence of the BPO Concentration on the Quercetin Inhibiting Effect[a]

Resin	H_{POHs}/H_0 0.5% BPO	H_{POHs}/H_0 2% BPO	G_{POHs}/G_0 0.5% BPO	G_{POHs}/G_0 2% BPO
POE1	16%	40%	75%	80%
POE2	18%	37%	81%	85%
PU1	26%	51%	82%	84%
PU2	29%	64%	54%	62%
PE	89%	96%	75%	78%

[a] Determination of the normalized parameters H_{POHs}/H_0 and G_{POHs}/G_0 for the hardness and the gel content. See Fig. 10 legend.

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References

1. Fouassier, J. P. Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications, Hanser Publishers: Munich, 1995.

2. (a) Stoye, D.; Freitag, W. In Resins for Coatings; Stoye, D.; Freitag, W., Eds.; Hanser Publishers: Munich, 1996; (b) Kice, J. L.; Polym, J Sci, Polym Chem Ed 19, 123, 1956.
3. (a) Burget, D.; Grotzinger, C.; Fouassier, J. P. Research Trends 7, 2001, 71; (b) Obeid, H.; Dossot, M.; Allonas, X.; Jacques, P.; Fouassier, J. P.; Dumarcay, S.; Merlin, A. Proc RadTech Eur 2003 Int Conf, Berlin, 2003, p 71; (c) Dossot, M.; Obeid, H.; Allonas, X.; Jacques, P.; Fouassier, J. P.; Merlin, A. J Appl Polym Sci 92, 1154, 2004; (d) Dossot M.; Sylla M.; Allonas X.; Merlin A.; Jacques P.; Fouassier J. P. J Appl Polym Sci 2000, 78, 2061.
4. Benavante-Garcia, O.; Castillo, J.; Lorente, J.; Ortuno, A.; Del Rio, J. A. Food Chem 68, 457, 2000.
5. Rice-Evans, C. A.; Miller, N. J.; Paganga, G. Free Radic Biol Med 20, 933, 1996.
6. Heim, K. E.; Tagliaferro, A. R.; Bobilya, D. J. J Nutr Biochem 13, 572, 2002.
7. Hotta, H.; Nagano, S.; Ueda, M.; Tsujino, Y.; Koyama, J.; Osakai, T. Biochim Biophys Acta 1572, 123, 2002.
8. Martin, F. PhD thesis, Université Henri Poincaré, Nancy, 1996.