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Photocatalysis and promoted photocatalysis during photocrosslinking of multifunctional acrylates in composite membranes immobilizing titanium dioxide [1]

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Abstract

The photocatalytic activities of semiconductor titanium dioxide (added to a standard titanium dioxide pigment) and five organometallic coordination compounds (containing cobalt(III) and vanadium(V) as central atoms) have been investigated during the photopolymerization and photocrosslinking of acrylic monomers, employed for the preparation of composite membranes by photografting onto a non-woven polyester support. By partly or wholly substituting the 30 wt.% titanium dioxide pigment with a semiconductor grade dioxide, the rate of decrease of unsaturation increases (by more than two orders of magnitude when substitution is complete). A strong photocatalytic activity is also shown by vanadium complexes. The rate of decrease of unsaturation can be fitted to a relaxation spectrum, the width of which depends on the chemical nature of the polymer network. The mean lifetime is a very sensitive measure of the photocatalytic effect. Multifunctional acrylic monomers (butanediol diacrylate, 1,6-hexanediol diacrylate and pentaerythritol triacrylate) are photoinitiated by 1,2-diphenyl-2,2-dimethoxyethanone in the presence of semiconductor and pigment grade titanium dioxide blends by the addition of organometallic coordination compounds as photocatalytic promoters. The results obtained in this investigation are in line with the relaxation model described above (also used successfully in previous studies), which interprets the photochemical reactivity during photocrosslinking in the presence and absence of photocatalytic promoters acting as efficient chain transfer agents. The photoinitiator 1,2-diphenyl-2,2-dimethoxyethanone alone is unable to carry out satisfactory polymerization in the presence of massive amounts of pigment grade titanium dioxide in the absence of semiconductor grade dioxide. The latter enhances strongly the rate of crosslinking, which is further increased by photocatalytic promoters. © 1997 Elsevier Science S.A.

Keywords: Composite membranes; Multifunctional acrylates; Photocatalysis; Photocrosslinking; Titanium dioxide

1. Introduction

The use of radiation-curable systems incorporating pigments is widespread and steadily increasing in many branches of technology. The difficulties associated with pigments and photoinitiators competing for incident light are well known and have been highlighted in a recent review [1]. A strong decrease in the radiation flux with increasing depth of profile is observed in these cases. This feature is responsible for through-cure problems, which are particularly relevant in applications concerning heavily pigmented coatings (using pigments which absorb strongly in the UV, such as titanium dioxide and carbon black) and in certain innovative operations (which use UV radiation to produce reinforced plastics and composite reactive membranes [2]). Most commercial and conventional photoinitiators fail in the last two applications in these extreme conditions of photopolymerization because of the strong interference of radiation absorption and diffusion by species to be immobilized or by reinforcing agents. Three essential conditions are demanded by these emerging technologies:

1. a required thickness much greater than that of ordinary coatings (from 200 μm to several millimetres);
2. a very high content of immobilized species (up to 35%–40%);
3. a need to keep irradiation times as low as possible (up to a few seconds) during membrane manufacture by photografting onto suitable supports so that the active surface area and other physicochemical properties of the immo-

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bilized species may be fully or almost fully maintained at the values obtained before grafting, i.e. the physicochemical behaviour must be practically the same as that of the free species.

Candidate photoinitiating systems suitable for this purpose either extend their near-UV absorption band to a suitable window of the visible spectrum (as wide as possible) or make appropriate use of photocatalysts and/or photosensitizers in a suitable window of the visible range. The latter approach has been used successfully [2–5] in previous work. In particular [4], the influence of photocatalytic systems, based on five different Co(III) and V(V) organometallic compounds, was evaluated by measuring the hardness as a function of the depth of profile in styrenated polyesters reinforced with 30 wt.% glass fibres. The performance of these compounds was also tested [4,5] during the photografting of membranes immobilizing 30 wt.% of titanium dioxide semiconductor. The photocatalytic activity of this type of titanium dioxide has been well studied in the literature, and these membranes show great promise in advanced oxidation processes carried out by photogenerated hydroxyl radicals for the degradation and mineralization of organic contaminants in wastewaters [6–11] and air [12], as well as for the induction of integral biodegradability in toxic and non-biodegradable organics [13].

In this paper, we investigate the photocatalytic activities of semiconductor titanium dioxide (added to a standard titanium dioxide pigment; composition of the blend varied from 0% to 100% semiconductor) and five organometallic complexes (photocatalytic promoters (co-photocatalysts)) in the photopolymerization and photocrosslinking of photoinitiated 1,4-butanediol diacrylate (BDDA), 1,6-hexanediol diacrylate (HDDA) and pentaerythritol triacrylate (PETIA) (model molecules of multifunctional acrylates) during the preparation of composite membranes by photografting onto a non-woven polyester support.

2. Experimental details

2.1. Materials

The titanium dioxide semiconductor (mainly anatase) was Degussa P-25 grade, whereas the standard pigment grade was that commonly used in the manufacture of paints. BDDA, HDDA and PETIA were kindly supplied by UCB (Drogenbos, Belgium) and were used as received without further purification or removal of small amounts of inhibitors. 2,2-Dimethoxy-1,2-diphenylethanone (Ciba Geigy, Switzerland) was used as standard photoinitiator, and its concentration was kept constant (10 wt.% with respect to the monomers) in all the runs.

2.2. Membranes

Membranes were prepared in a pilot plant operating continuously by photografting 200 ± 15 g m^{-2} of a blend containing the monomers, the photoinitiator and 30 ± 3 wt.% of a mixture of P-25 and standard pigment grade titanium dioxide (variable ratio between these two kinds of titanium dioxide). Photografting onto a non-woven polyester support was carried out in standard conditions with an irradiation intensity of 2.5×10^{-5} einstein s^{-1} cm^{-2}. The final porosity of the photosynthesized membranes was regulated at 2–4 μm in the optimal conditions of photocrosslinking by controlling the rheological parameters of the blend employed for membrane manufacture. When the photocrosslinking rate was low or very low, the porosity could fall to 0.02–0.1 μm. Air was not excluded during the plant operation.

In all of the blends, in addition to semiconductor titanium dioxide, varying amounts of proprietary photocatalysts (I–V) (Chimia Prodotti e Processi, Milan, Italy) were added in order to sensitize the semiconductor dioxide outside its optical absorption range at wavelengths greater than that corresponding to the band gap. These photocatalysts were composed essentially of stabilized preparations containing the following organometallic compounds:
triethylvanadate(V) (**I**);
oxo-(diquinolyloxo)vanadic(V) acid (**II**);
μ-peroxo-bis[*N*,*N*′-ethylene-bis(salicylideneiminato)-cobalt(III)] (**III**);
μ-peroxo-bis[*N*,*N*′-ethylene-bis(salicylideneiminato)-dimethylformamide cobalt(III)] (**IV**);
synergic mixture of tri-(tert-butyl)- and tri-(isopropyl)-vanadate(V) (**V**).

As the only information available on these photocatalytic systems was their nominal concentration of photoactive species, they were used as supplied on the basis of this nominal concentration.

2.3. Procedures

In order to assess quantitatively the influence of the ratio between P-25 and pigment grade titanium dioxide and the concentration of the promoting photocatalysts (**I–V**) on the photopolymerization and photocrosslinking rates, the analysis of the residual unsaturation during photocrosslinking was measured for photografted membranes, starting from a degree of conversion of double bonds in the grafted layer of 0.60–0.65. These investigations were performed by carrying out kinetic tests as a function of time, using multiple internal reflection spectroscopy, following a standard technique employed in previous work [2,3,14]. Microtomized sections of the membranes were employed for analysis to obtain information integrated over the deep layers of the membranes and not only on the top surface. Kinetic data were fitted by the relaxation model

$$C_t/C_0 = \exp[-(t/\tau)^{\beta}] \qquad (1)$$

where the concentration (C) ratio (in which the subscript t denotes the irradiation time, starting from the "zero" time corresponding to a degree of conversion of double bonds of 0.60–0.65) represents the empirical relaxation function, the β parameter is the width of the relaxation spectrum and τ is the mean lifetime.

3. Results and discussion

The main requirement for the photopolymerization of systems composed of heavily pigmented coatings or of composite membranes, such as those examined in this study, is a fast photoreactivity, which should not be confined to the exposed areas, but should penetrate, as rapidly as possible, to the depth of the whole profile. For this challenging situation, the most promising candidates are monomers which are photopolymerized by radicals. Acrylic monomers are attractive because of their high reactivity, low volatility and moderate cost. The appropriate choice of photoinitiating system is of paramount importance. It has been shown in Ref. [8], by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) studies, that trapped radicals are present in a crosslinked polymer after irradiation; they have been identified [8] as radicals at tertiary carbon atoms derived from hydrogen abstraction. The occlusion of these macromolecular radicals represents termination, because the lifetimes of these radicals are very long and their thermal polymerization is very sluggish, except at very high temperatures [15]. A slow polymerization takes place in the dark, since few unreacted monomers and, more importantly, dangling double bonds are present in photocrosslinked polymers [8,16]. The reactivity of these macroradicals, even at room temperature, may be greatly enhanced [3,4,14] by the addition of suitable photocatalysts. The photocatalytic system does not affect the value of β both during and after irradiation, as shown by the relaxation model given in Eq. (1), which has been found to be verified up to 100% conversion of the double bonds [3,4,14–16]. This parameter is a characteristic of the polymer network being photocrosslinked, and reflects the crosslinking pattern of the polymer, irrespective of whether crosslinking is carried out thermally or by photochemical activation (use of photocatalysts). In contrast, a very sensitive parameter indicating the action and performance of photocatalytic systems is τ, the value of which is greatly modified by the presence of an active photocatalyst and its concentration.

Photocatalytic activation is preferable to thermal activation, since prohibitively high temperatures would be needed to reach the crosslinking rates required for the applications in this study and careful post-curing would be needed to drive the polymerization to the highest possible degree of cure.

The validity of the model expressed by Eq. (1) has been confirmed by all the experimental results reported here, which yield a practically constant value of β in all the kinetic runs pertinent to the same monomer (0.35 ± 0.03, 0.38 ± 0.03 and 0.48 ± 0.03 for BDDA, HDDA and PETIA respectively, the uncertainly being expressed as the probable error of all the runs). The model is also confirmed by the very variable values of the mean lifetimes τ, which are collected in Tables 1–3 for the three monomers above for the different conditions in which the photografting of the composite membranes was carried out. In the tables, the mean lifetimes were obtained by plotting the kinetic data in the form of double natural logarithms (ln.ln) of the concentration ratio of the double bonds (at times t and zero respectively) as a function of ln t. Following the form of Eq. (1), from this plot $-\beta$ was obtained as the slope and $\beta \ln \tau$ as the intercept. The τ values are reported in Tables 1–3 as a function of the weight fraction f of P-25 semiconductor oxide in the titanium dioxide mixture used (semiconductor grade and pigment grade dioxide, with the fraction f of the former varying between 0.00 and 1.00). The mean lifetime values are also reported in Tables 1–3 as a function of the concentration of the photocatalytic promoters I–V, the latter being expressed as parts per million of coordinated atom in the blend.

Some experimental observations can be made from an examination of the results in Tables 1–3.

Table 1
Mean lifetimes τ (min) evaluated by Eq. (1) from the kinetic data obtained during the photocrosslinking of BDDA in membranes immobilizing 30 ± 3 wt.% of titanium dioxide at various values of f (weight fraction of P-25 grade semiconductor dioxide to total dioxide) and concentrations C_{cat} of the photocatalytic promoters I–V (expressed as parts per million of coordinated atom (cobalt or vanadium) in the photografted blend)

Concentration (ppm)	f				
	0.00	0.10	0.20	0.50	1.00
$C_{\mathrm{cat}} = 0.00$	12.3	5.46	2.73	0.59	0.07
$C_{\mathrm{cat\,I}} = 550$	2.07		1.38		
$C_{\mathrm{cat\,II}} = 550$	1.68		1.16		
$C_{\mathrm{cat\,V}} = 100$	0.87		0.71		0.04
$C_{\mathrm{cat\,V}} = 550$	0.63		0.29		0.02
$C_{\mathrm{cat\,V}} = 3000$	0.63		0.28		0.02
$C_{\mathrm{cat\,III}} = 3000$	12.1		2.70		
$C_{\mathrm{cat\,IV}} = 3000$	11.8		2.67		

Table 2
Mean lifetimes τ (min) evaluated by Eq. (1) from the kinetic data obtained during the photocrosslinking of HDDA in membranes immobilizing 30 ± 3 wt.% of titanium dioxide at various values of f (weight fraction of P-25 grade semiconductor dioxide to total dioxide) and concentrations C_{cat} of the photocatalytic promoters I–V (expressed as parts per million of coordinated atom (cobalt or vanadium) in the photografted blend)

Concentration (ppm)	f				
	0.00	0.10	0.20	0.50	1.00
$C_{\mathrm{cat}} = 0.00$	13.8	5.68	2.94	0.65	0.08
$C_{\mathrm{cat\,I}} = 550$	2.16		1.52		
$C_{\mathrm{cat\,II}} = 550$	1.87		1.29		
$C_{\mathrm{cat\,V}} = 100$	0.95		0.80		0.05
$C_{\mathrm{cat\,V}} = 550$	0.66		0.30		0.02
$C_{\mathrm{cat\,V}} = 3000$	0.65		0.29		0.02
$C_{\mathrm{cat\,III}} = 3000$	13.0		2.86		
$C_{\mathrm{cat\,IV}} = 3000$	12.7		2.81		

Table 3
Mean lifetimes τ (min) evaluated by Eq. (1) from the kinetic data obtained during the photocrosslinking of PETIA in membranes immobilizing 30 ± 3 wt.% of titanium dioxide at various values of f (weight fraction of P-25 grade semiconductor dioxide to total dioxide) and concentrations C_{cat} of the photocatalytic promoters I–V (expressed as parts per million of coordinated atom (cobalt or vanadium) in the photografted blend)

Concentration (ppm)	f				
	0.00	0.10	0.20	0.50	1.00
$C_{cat} = 0.00$	15.2	6.28	3.76	0.73	0.09
$C_{cat\,I} = 550$	2.45		1.63		
$C_{cat\,II} = 550$	2.12		1.41		
$C_{cat\,V} = 100$	1.04		0.93		0.06
$C_{cat\,V} = 550$	0.75		0.36		0.03
$C_{cat\,V} = 3000$	0.68		0.34		0.03
$C_{cat\,III} = 3000$	14.8		3.51		
$C_{cat\,IV} = 3000$	14.6		3.44		

1. By partly or wholly substituting the titanium dioxide "pigment" with semiconductor grade dioxide, a marked increase in the photopolymerization rate is produced. This effect on the rate reaches two orders of magnitude when pure semiconductor is used. This means that semiconductor grade titanium dioxide also possesses a marked photocatalytic activity on the photocrosslinking rates.
2. In the photoreactive blend used in this work, in addition to the activity of semiconductor grade titanium dioxide, a marked efficacy of vanadium complexes is noted, which is particularly relevant for photocatalyst V, as observed from its action on blends with $f = 0.00$ (without the addition of semiconductor grade dioxide). The performance of V is remarkable. It may be realized by considering that 3000 ppm of vanadium in the form of coordination compound V is sufficient to photopolymerize a 200 g m^{-2} coating, pigmented with as much as 30 wt.% of titanium dioxide pigment, with a mean lifetime of about 0.7 min. This is not an acceptable industrial rate for pigmented coatings, since it would require an exceptionally long radiation tunnel or radiation times of several minutes; nevertheless, it stresses the efficiency of vanadium complexes. The standard photoinitiator alone would be practically unable to photopolymerize the same coatings. In contrast with vanadium, cobalt complexes, which are very active in styrenated resins [5], have little effect on the acrylic monomers employed in this work.
3. The vanadium photocatalysts I, II and V may also act as photocatalytic promoters or co-photocatalysts, i.e. they can enhance the action of semiconductor grade dioxide photocatalyst when present. This is shown by the mean lifetimes measured with $f = 0.20$. Here again, the activity of the cobalt(III) coordination compounds is almost negligible.
4. The photocatalytic activity in the presence of V shows a saturation effect when the concentration of the photocatalyst is increased above a certain value (see the data in Tables 1–3 concerning the runs at $f = 0.00$). This behaviour is expected. In a previous study [14], a threshold effect at low concentrations was observed; this was not very evident in the data of this work, mainly because few data have been obtained as a function of concentration.

The most suitable physical model which can be used to explain Eq. (1), as reported in previous studies [2–4,14–16], is to consider the double bonds as more or less shallow traps which can transfer to radical sites; the photocatalysts act as chain transfer agents. As long as the photopolymerization reaction proceeds, the traps are deepened, so that the relaxation times increase continuously. The greater the molecular weight of the radicals, the deeper the traps. The mechanism of action of photocatalysts I–V probably involves the facilitation of the transport of macromolecular radical sites by hydrogen transfer. In the case of titanium dioxide semiconductor as photocatalyst, the transport concerns either low molecular weight radical species (such as hydroxyl radicals or other labile oxygen radical species, generated at the surface of semiconductor particles by the reaction of photogenerated holes with adsorbed water molecules) or higher molecular weight radicals (macromolecular radicals, formed by direct reaction between the photogenerated holes and monomer molecules at the beginning of polymerization or the pendant acrylate groups of the macroradicals during photocrosslinking). In this way, the height of otherwise insurmountable barriers is drastically decreased. From this point of view, it is significant that the active photocatalysts I–V, whether they operate alone or as co-photocatalysts, are oxygen activators by radical mechanisms and/or facilitated transport agents for oxygen or labile oxygen radical species. In the presence of titanium dioxide with strong semiconductor activity, photogenerated electrons may also participate [17–20] to yield very reactive hydroperoxy radicals with oxygen or oxygen donors, together with other labile oxygen species [19], thus activating the redox reactions which may take place in a complex system, such as that considered in this paper, in which oxygen is present. Indeed, if water adsorbed onto titanium dioxide semiconductor can be regarded as an effective electron–hole recombination centre [20], the adsorbed oxygen can be considered as an effective electron trap to prevent such a recombination process. In contrast, the presence of adsorbed water, either vapour or liquid, on photocatalytic titanium dioxide may help to remove eventual surface species poisoning the catalyst [21]. Consequently, in the presence of titanium dioxide semiconductor and co-photocatalysts, it is not unrealistic to assume that the combined effects of the mechanisms given above result in an increase in the rate of trapped radical decay with extensive crosslinking.

A further advantage is obtained by the use of these photocatalytic systems. Efficient operations may be carried out without the exclusion of air from the system. Labile oxygen radical species, photocatalytically produced, lead to fast reactions which decrease the unsaturation of the photopolymer, both by inducing reactivity on residual monomer molecules and by facilitating crosslinking by pendant acrylate groups present in the growing polymer network. Even if the permanence of a certain amount of bound oxygen in the final polymer may be inferred, from the practical point of view, this has not caused any inconvenience in the prolonged activity of the functionalized photocatalytic membranes prepared by this technique. During more than 4 years of pilot-plant experience [6–13] and in drastic photochemical conditions (UV irradiation), the photocatalytic membranes have only been replaced twice a year or so, and not because of the breakdown of the polymer structure by photodegradation.

Finally, with regard to the β values, for BDDA and HDDA they have been found to coincide strikingly with those measured in previous work [3,15] during grafting or bulk photopolymerization. The similar values may be attributed to the similar polymer structures, although BDDA exhibits a greater rigidity than HDDA, as shown by EPR/ENDOR measurements of the ratio between the integrated spectral area of the single-line and three-line signals of trapped macroradicals [8,15,16], due to the smaller number of methylene groups linking the two acrylate functions. In fact, increasing the number of methylene bridges enhances rotation. For PETIA, the larger value of the β parameter may be ascribed to the different crosslinking pattern (trifunctional derivative).

4. Conclusions

1. The results obtained in this investigation are in line with a relaxation model, used successfully in previous studies, which interprets the photochemical reactivity during photocrosslinking in the presence and absence of photocatalysts acting as chain transfer agents. It is suggested that the production of labile oxygen radical species may provide an important contribution to this mechanism. This stems from the fact that the addition of semiconductor grade titanium dioxide enhances strongly the rate of photocrosslinking. The activity of the semiconductor may be increased further by co-photocatalysts (photocatalytic promoters), i.e. suitable coordination compounds, the choice of which depends on the nature of the pre-polymer system. These photocatalysts can yield industrially acceptable rates of photopolymerization also in the presence of massive amounts of pigment grade titanium dioxide. A decrease in unsaturation, up to 95% conversion or more, occurs in reasonable times.
2. The physicomathematical model is characterized by the fact that the relaxation spectrum is defined by two parameters: a width, of less than unity, depending exclusively on the chemical nature of the pre-polymer system, and a mean lifetime, which is a very sensitive measure of the rate spectrum and, consequently, of the kinetic performance of the photocatalytic system.
3. Finally, the use of photocatalytic systems, such as those investigated in this work, will allow radiation curing to be carried out very efficiently in the presence of oxygen. The outstanding increase in the monomer consumption and photocrosslinking rate brought about by suitable photocatalysts easily compensates for any deleterious action due to the incorporation of bound oxygen into the polymer structure, at least for the applications envisaged in this paper.

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