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Fluorescent Probes for Monitoring the UV Curing of Acrylic Adhesives, 1.

FTIR and Fluorescence in Real Time

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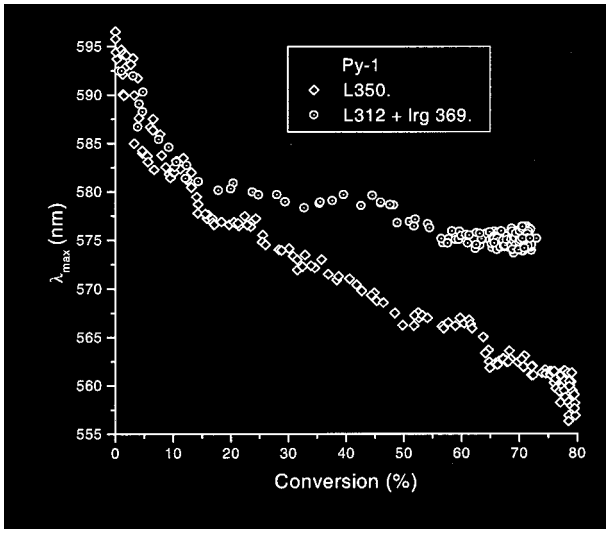
The use of the fluorescence technique for monitoring the UV-curing of two polyurethane-based adhesives containing acrylic monomers is described in this paper. The increase of the fluorescence intensity as well as the maximum wavelength shift on emission was measured in real time during the photopolymerisation pro-cess. The established relationship between fluorescence and conversion allowed monitoring of the course of the process beyond vitrification. In that sense, all the fluorescent probes studied were sensitive to the formulation curing and in some cases, the range of conversions in which they were useful was limited by their size and probably, by the free volume fraction in the polymeric matrix. Moreover, polymerisation rates were obtained from fluorescent kinetic profiles and used to carry out a comparative study of the different photosensitive formulations.

The real time FTIR (RTIR) results show the highest photoinitiation efficiency of the photoinitiator 2-benzyl-*2-N,N*-dimethylamino-1-(4-morpholinophenyl)-1-butanone (Irgacure 369) compared to that of 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651). The limitation of RTIR method for monitoring slow post-reactions was overcome by the use of the fluorescence-based method. Thus, a fluorescence intensity increase and a blue-shift of the emission band were measured after the limiting conversion was attained. Dynamic mechanical analysis showed that the glass transition temperature of the polymer increases during prolonged exposure to irradiation confirming the increase of the system rigidity.



Maximum wavelength shifts of pyridine-1 versus conversion during UV-curing of L350 (used as received) and L312 (with Irg369).

Introduction

Recently, society has become aware of the necessity to reduce or eliminate VOC (volatile organic components) emissions from coating applications. These reasons together with the growing demand for adhesive use in technologies and speciality applications have led chemists to look for alternatives to the traditional solvent-based adhesives. Radiation-cured adhesives, by means of EB (electron beam) or UV-light, have been developed and show the potential to replace conventional solvent-based systems that are ozone-depleting. UV-curing adhesives include a photoinitiator in the formulation which under irradiation absorbs and converts UV-visible light into reactive intermediates, such as free radicals and radical ions, and/or long lived intermediates, such as acids or bases, which initiate the photochemically driven polymerisation that is normally completed in few seconds. Moreover, the advantages of UV-curing technology such

as cost saving, high manufacturing efficiency and environmental benefits are expected to be evaluated with a view to replacing conventional methods. For these reasons great effort has been made by industry to develop new photocurable adhesives and a large number of them are patented every year. On the other hand, scientific researchers have not devoted much interest to this applied field[1–4] and the knowledge is, mainly, based on experimental developments.

Two considerations have to be taken into account when implementing UV-curing adhesives technologies that include the light absorbing or reflecting properties of the substrates as well as any post-curing effect that might alter the performance characteristic of the adhesive bonds. In that sense it would be worthwhile to have a method to determine the degree of cure independently of the curing conditions. Over the past few years, fluorescence-based methods have shown their ability to monitor thermal and photochemically induced curing.[5–8] In addition, they are "user-friendly" technologies that have a profound effect on the performance and cost of manufactured goods, on processes, and on the quality of life as related to environmental issues.

The origin of the fluorescence emission can stem from the adhesive formulation components[9] or from an extrinsic fluorescing compound, which is called a fluorescent label or probe depending on whether it is chemically linked or physically dispersed into the polymer matrix, respectively. Moreover, different types of fluorescent probes have been used for monitoring the cure of resins.[10–14] Among them, TICT (twisted intramolecular charge transfer) fluorescent probes show multiple fluorescence which has been explained by the existence of different excited states.[15, 16] The excited state initially reached, with a planar conformation relaxes by single bond twisting in the excited state accompanied by charge transfer from electron donor to acceptor moieties. The introduction of further double bonds extends the possibility of twisted conformers. In most of the cases, those excited states show a non-emissive character due to the small energy gap between ground and excited states. Temperature and some properties of the surrounding medium such as viscosity, influence this rotational motion. Thus, these twistable probes exhibit a simultaneous fluorescence dependence on polarity and free volume effects. The emission efficiency is low in polar and fluid media and increases with rigidity/viscosity.[17] Fluorescence sensitivity usually decreases at the higher temperatures used for thermal cure, and thus UV-curing, which normally is carried out at room temperature, is very attractive for heat-sensitive probes.

The goal of this paper is to establish a correlation between fluorescence and conversion during UV-curing of acrylic adhesives. The results from following the fluorescence of selected probes during the entire range of curing of acrylic adhesives are presented here. The change of fluorescence parameters (intensity and maximum wavelength) has been followed during the photocuring of the adhesives under UV-irradiation from a conventional medium-pressure mercury lamp (steady-state irradiation). RTIR has been used to measure the conversion reached at different irradiation times. Linear correlations between fluorescence intensity and conversion have been obtained for some fluorescent probes during UV-curing. Also, fluorescence band shifts have been detected during photopolymerisation, and the volume occupied by the fluorescent probe appears to be the parameter that would determine the sensitivity of the probe to detect the changes in viscosity/polarity occurring during UV-curing. Moreover, post-polymerisation reactions have been investigated by fluorescence and dynamic mechanical analysis.

Experimental Part

Fluorescent Probes and Acrylic Adhesives

Six synthesised fluorescent probes are shown in Figure 1. The synthesis of these compounds is described elsewhere.[18, 19] Also, four fluorescent commercial probes, from Aldrich, (Figure 2) were selected to follow the photopolymerisation reaction of the acrylic systems.

The adhesive formulations were provided by the Loctite Corporation. Loctite 350 (L350) is a UV-curable acrylic adhesive containing a photoinitiator while Loctite 312 (L312) requires a further addition of an activator for UV-curing. Both adhesive formulations are based on polyurethane methacrylic resins and a mixture of acrylic monomers as reactive diluents. L312 contains 50–55 wt.-% of the resin and 35 wt.-% of hydroxypropyl methacrylate, acrylic acid (5–10 wt.-%), a substituted silane (0.1–1 wt.-%) and tri-

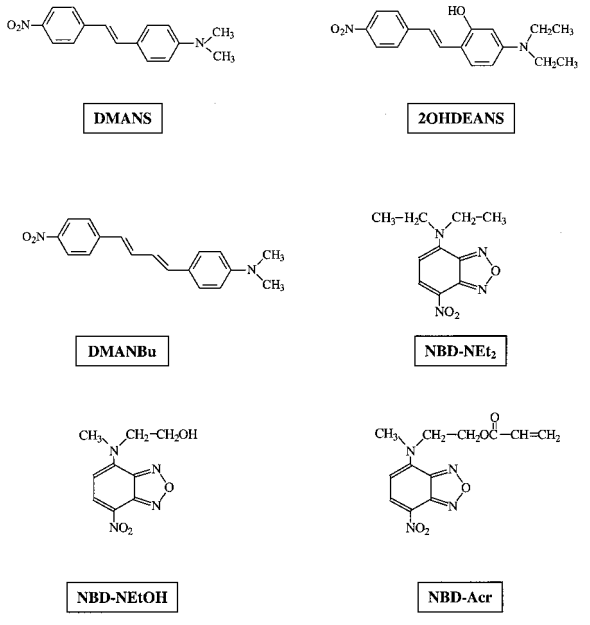
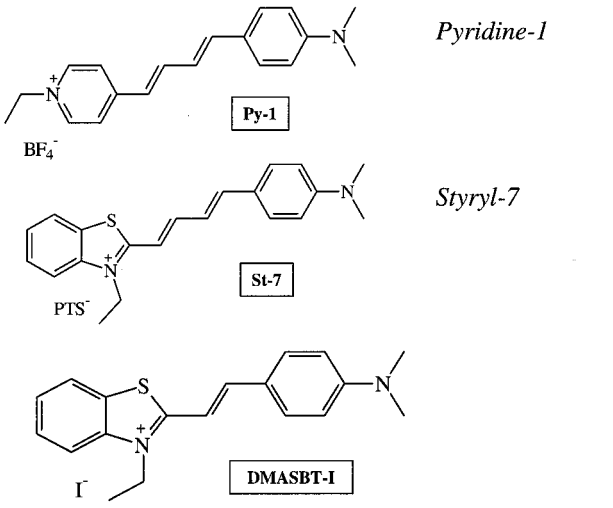
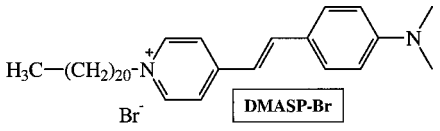


Figure 1. Structures of the synthesised fluorescent probes.



2-[4-(dimethylamino)styryl]-3-ethyl benzothiazolium iodide



2-[4-(dimethylamino)styryl]-1-docosylpyridinium bromide

Figure 2. Structures and names of the commercial fluorescent probes of D-π-A$^+$X$^-$ salt type.

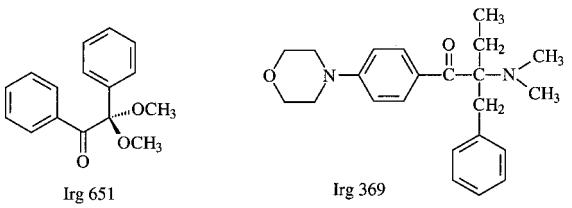


Figure 3. Structures of the commercial photoinitiators.

butylamine (0.1–1 wt.-%). L350 contains 35–40 wt.-% of the resin and 15–20 wt.-% of hydroxypropyl methacrylate, 15–20 wt.-% of lauryl methacrylate (LMA), methyl methacrylate (15 wt.-%) and acrylic acid (5 wt.-%).

The commercial photoinitiators 2-benzyl-2-*N,N*-dimethylamino-1-(4-morpholinophenyl)-1-butanone (Irgacure 369) and 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651), from Ciba Speciality Chemicals, were selected to carry out the UV-curing of L312 and their structures are shown in Figure 3.

Sample Preparation

Samples of the adhesive formulations containing fluorescent probe (0.03 wt.-%) and photoinitiator (1 wt.-%) were prepared by stirring all components until homogeneous solutions were obtained (8 h). L350 already contains a photoinitiator and no addition was required in this case. The photocurable formulations were cast as a uniform layer coating on a polyethylene film (or an aluminium foil for FTIR measurements), and then covered with a low density polyethylene film (LDPE, 40 μm thick), which does not absorb at the IR frequencies selected to follow the photopolymerisation reaction nor at the excitation/emission and UV-irradiation wavelengths. The role of the LDPE film was to prevent oxygen diffusing from the atmosphere into the sample during the irradiation at room temperature. Photosensitive coatings of 10 μm thickness were obtained by controlled pressing.

The photoinitiators employed also absorb at the excitation wavelength (355 nm), however fluorescence from the photoinitiators do not interfere the fluorescence spectra of the probe due to their low fluorescence quantum yields.

Monitoring the UV-Curing of Acrylic Systems

Adhesive samples were photopolymerised at room temperature with polychromatic continuous light under air atmosphere up to their limiting conversion. For all samples, the disappearance of double bonds and the fluorescence changes of the probes were monitored by means of two techniques: FTIR and fluorescence spectroscopy both in real time conditions. Moreover, dynamic mechanical analysis was carried out at different irradiation times.

Real Time Fluorescence Spectroscopy

A scheme of the device designed is shown in Figure 4.

A Nd-YAG laser (Quanta-Ray from Spectra Physics) emitting at 355 nm (laser pulse width = 6 ns) was directed through two laser mirrors (Lambda Research Optics, Inc.) at 45° to the sample. The laser beam was expanded by using a PCV fused silica lens to overfill the image of the fluorescent probe (about 4 cm diameter). An attenuator was used to

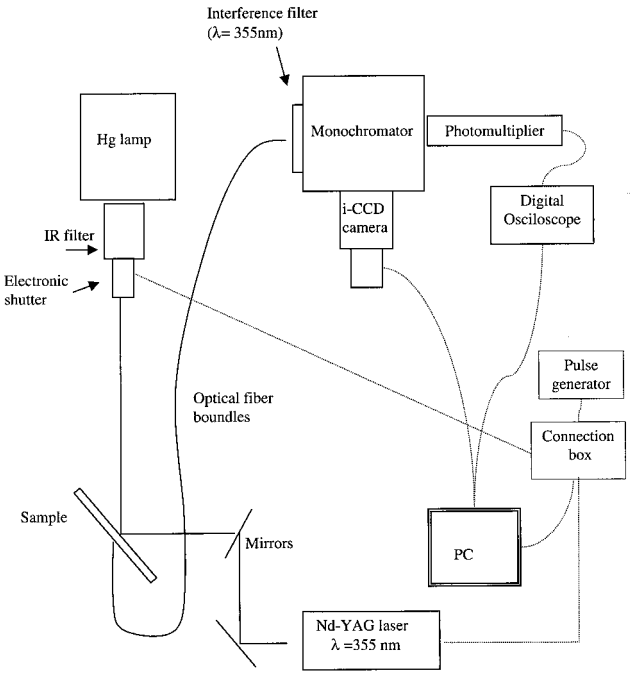


Figure 4. Scheme of the system employed to carry out the Fluorescence Spectroscopy in Real Time for monitoring the UV-curing of the acrylic adhesives.

avoid initiation of polymerisation by the excitation laser beam used for analysis. Laser output reaching the sample, measured by a photocalorimeter Scientech model H310D, was 0.4 mW/cm^2.

A fibre optic placed at 45° with respect to the sample collected fluorescence emission to a monochromator (Oriel MS257). A cut-off filter (355 nm) was used to eliminate laser beam interference. The spectra were recorded by means of an intensified CCD camera, Andor ICCD-408, using an exposure time of the camera of 1 μs. UV-curing was carried out simultaneously by irradiation at 135° with polychromatic light from a 400 W mercury lamp (Macam-Flexicure irradiation system) focused through a light guide on the adhesive formulation. The incident light intensity was measured by actinometry[20] using a film of poly(methyl methacrylate) containing Aberchrome 540, $I_0 = 1.47 \times 10^{-10}$ Einstein/s. Because UV-curing is a very rapid reaction occurring in few seconds, the frequency of the laser pulse was selected at 3.3 Hz to monitor the whole photopolymerisation process. Furthermore, no photodegradation of the probe was observed under these experimental conditions.

The trigger of the intensified CCD camera and laser were controlled by a pulse delay generator, Stanford model DG 535. The acquisition and preliminary manipulation of data was carried out by means of the Oriel software "IntraSpec V" that allows storage and processing of data.

FTIR in Real Time (RTIR)

RTIR measurements were carried out in a Nicolet 520 infrared spectrophotometer provided with a Fourier Transformed algorithm. The irradiation was carried out using the Macam-Flexicure system equipped with a medium pressure mercury lamp Sylvania (400 W) and an electronic shutter. The UV light was conducted through a flexible light guide to the IR compartment. The end of the optical fibre was positioned to focus the UV-irradiation at a 45° angle onto the sample. The samples were placed over a specular reflection accessory (SPECAC) in the infrared spectrophotometer where they were simultaneously exposed to the UV-light and the IR analysing beam. The incident light, measured by actinometry, reached the same value as that of the real time fluorescence device.

FT-Infrared spectra (4 cm^{-1} resolution) were recorded at different irradiation times. The spectrophotometer was operated in the absorbance mode and the detection wavenumber was set at 817 cm^{-1} to monitor the disappearance of the acrylate double bond. The decrease in the absorbance was analysed by means of a software programme to record data in real time. Because the IR absorbance is proportional to the monomer concentration, conversion versus time profiles were directly obtained from the recorded spectra. The degree of cure, α, can be expressed by Equation (1):

$$\alpha = \frac{(A_0 - A_t)}{A_0} \quad (1)$$

where A_0 is the initial absorbance at the chosen frequency and A_t is the absorbance value at the irradiation time t. The slope of the plot of the degree of cure versus time is proportional to the polymerisation rate.

Dynamic Mechanical Analysis (DMA)

The tensile dynamic mechanical spectra (storage modulus E', loss modulus E'' and loss factor $tan\delta$) of the UV-cured adhesives were obtained in a Dynamic Mechanical Analyzer DMA 983 from TA Instruments. The measurements were carried out in flexion mode between −50°C and 180°C using a heating rate of 5°C/min at a fixed frequency of 1 Hz (amplitude 1.2 mm). The probes were parallelepipedic bars of dimensions 0.12 × 3 × 6 mm^3. The data were collected in a Thermal Analyst 3100 TA Instruments connected to the unit DMA 983.

Instrumentation

UV spectra were recorded by means of a Shimadzu UV-265-FS spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer LS-50B spectrofluorimeter. All the spectra were corrected by the spectrofluorimeter curve response. The determination of fluorescence quantum yields was performed using the relative method with quinine sulphate as standard.[21] Solvents were of spectroscopic or analysis grade.

Results and Discussion

In this work we have used ten fluorescent probes for monitoring UV-curing of two adhesive formulations, L350 and L312, by real time fluorescence and infrared spectroscopy. The aim was to find a correlation between fluorescence and the extent of the UV-curing reaction, determined by conventional methods. All probes showed sensitivity towards acrylic double bond conversion during polymerisation reaction, and in general at least one of the emission parameters changes during the curing reaction. For these reasons, we mainly present results on L350 with discussion of other where relevant.

RTIR

RTIR was used to monitor the decrease of the absorbance of the band at 817 cm^{-1} due to the disappearance of the acrylate double bond during the UV-curing.

The kinetic profiles obtained for the polymerisation of the acrylate adhesives, L350 (used as received) and L312 using two different photoinitiators, are shown in Figure 5. In order to compare the behaviour of the different adhesive formulations two parameters were determined from the corresponding conversion-irradiation time curves:

- The initial polymerisation rate, obtained from the slope of the initial linear portion of the corresponding curves, R_p, expressed in s^{-1}.
- The final conversion defined as the extent of cure attained when the polymerisation reaction ends or reaches a plateau, α_f.

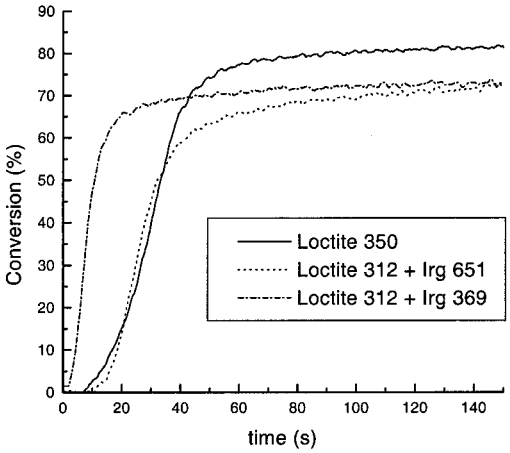


Figure 5. RTIR kinetic profiles of UV-curing of L350, used as received, and L312, using two different photoinitiators, Irg369 and Irg651.

The shape of the curves resembles the common behaviour of free radical polymerisation, an induction period at the beginning of the UV-curing process, showing dependence on the nature of the adhesive formulation, and a rapid first stage followed by a slow evolution. High degree of cure is reached in less than 50 s (20 s in the case of L312-Irg369); the slow stage is due to monomer consumption under restricted mobility of the radicals, as a consequence of the vitrification process, that leads to a decrease in the rate of the termination reactions. Thus, the vitrified polymer generated during the fast stage contains a residual amount of unsaturations and trapped radicals.

In Table 1, the values of the polymerisation rates, R_p, and the final conversion, α_f, are compiled under our experimental conditions of irradiation. Both the polymerisation rates and the limiting conversions are dependent on the photocurable formulation and thus, L350 reaches a higher degree of cure than L312. The morpholino moiety of the photoinitiator Irg369 improves the photoinitiation efficiency in comparison with that of Irg651 and the polymerisation rate is double for the former formulation.

The influence of the fluorescent probes in the photopolymerisation kinetics was checked. In general the same polymerisation rates were obtained when UV-curing of L350 was carried out in the presence of different fluorescent probes. Slight differences in the final degree of cure fall within the range of experimental error. Similar behaviour was also observed for L312 using Irg369 as photoinitiator. However, UV-irradiation of adhesive formulations containing Irg651 gives rise to quenching the fluorescence of the probes. For this reason, this photoinitiator was not convenient for our purposes. This can be related to the fact that photobleaching of the fluorescent probes may occur in the presence of sensitisers. Similar problems were found by other authors.[22] Hence, the importance of the selection of both components, the photoinitiator and the fluorescent probe, has to be pointed out.

Table 1. Polymerisation rates, R_p, and final degrees of cure, α_f, of UV-cured adhesives L312 and L350.

UV-curable adhesive	Photoinitiator[a)]	$\frac{R_p}{s^{-1}}$	$\frac{\alpha_f}{\%}$
L350	–	2.5	81
L312	Irg 369	5.8	74
L312	Irg 651	2.9	75

[a)] L350 was used as received with a commercial photoinitiator included in the formulation.

Selection of the Fluorescent Probes

The selection of fluorescent probes is a crucial issue and different parameters such as fluorescence quantum yield and overlapping of the emission spectrum with that of the adhesive formulation were considered. Ten fluorescent probes were used in this work where six of them were synthesised and the others were commercial. The structures of the synthesised fluorescent probes are shown in Figure 1 together with those used in this paper. Their common feature is to have a D-π-A structure type where A and D are electron acceptor and donor moieties, respectively. Moreover, the donor group is a dialkylamino and the acceptor is a nitro group. Two different π systems were derived: a diarylpolyene and the NBD-chloride (4-chloro-7-nitrobenz-2-oxa-1,3-diazole). The NBD moiety has been widely used for labelling biological substrates[23] and in this work, non-reactive and reactive derivatives were prepared. It is expected that different photophysical behaviour will be shown for these fluorescent compounds used either as probe or label. In the case of diarylpolyene derivatives, the introduction of the alkylamino group reduces the quantum yield of *trans* → *cis* photoisomerisation and, in general, increases the fluorescence quantum yields, even though both processes are competitive deactivation pathways for the excited states of these molecules. The commercial fluorescent probes used in this work, are salts of the D-π-A^+X^- type (Figure 2), containing pyridinium and benzothiazolium groups that improve compatibility in polar media. The solubility of these probes is limited in nonpolar surroundings and hence, DMASP-Br includes a long alkyl chain to extend the solubility in less polar resins. They can be considered as stilbene-like molecules in which a positive charge is introduced by quaternization. Jager et al.[24] have reported the use of other organic donor-π-acceptor salts for monitoring photopolymerisation reactions of dimethacrylates. It was pointed out that the position of the pyridinium cation, the number of double bonds and the anion nature would influence their photophysical behaviour.

Table 2. Absorption and fluorescence emission properties of the selected fluorescent probes in different solvents at room temperature.

Probe	Abs./λ_{max}	Fluorescence/λ_{max}(ϕ_F)					
	nm	nm					
	THF	Hexane[a)]	Ether[a)]	THF	EtAcO	EtOH[a)]	Water[a)]
DMANS	419	495 (0.12)	565 (0.18)	616 (0.01)	612 (0.01)	i.s.	i.s.
2OHDEANS	459	513 (0.07)	575 (0.10)	617 (0.01)	615 (0.01)	i.s.	i.s.
DMANBu	447	522 (0.16)	597 (0.04)	651 ($<10^{-3}$)	641 ($<10^{-3}$)	i.s.	i.s.
NBD-NEt_2	473	516 (0.18)	513 (0.08)	526 (0.01)	522 (0.01)	i.s.	i.s.
NBD-NEtOH	475	i.s.	519 (0.12)	528 (0.02)	530	531 (0.007)	542 (0.001)
NBD-Acr	469	497 (0.10)	511 (0.15)	521 (0.08)	521 (0.09)	(0.03)	i.s.
Py-1	478	i.s.	i.s.	645	636	648	645
St-7	570	i.s.	i.s.	689	678	682	675
DMASBT-I	537	i.s.	i.s.	598	598	591	592
DMASP-Br	456	i.s.	i.s.	580	580	596	i.s.

[a)] i.s.: insoluble.

Table 3. Stokes shifts of the selected fluorescent probes.

Probe	Stokes shift / cm^{-1}					
	Hexane[a)]	Ether[a)]	THF	EtAcO	EtOH[a)]	Water[a)]
DMANS	3952	6224	6860	7079	i.s.	i.s.
2OHDEANS	4036	5233	5579	6061	i.s.	i.s.
DMANBu	4539	6185	7010	7126	i.s.	i.s.
NBD-NEt_2	2842	2105	2130	2029	i.s.	i.s.
NBD-NEtOH	i.s.	2471	2113	2318	2077	1549
NBD-Acr	2595	2360	2128	2451	i.s.	i.s.
Py-1	i.s.	i.s.	5417	5690	5186	7485
St-7	i.s.	i.s.	3030	3044	2789	2978
DMASBT-I	i.s.	i.s.	2110	2253	1983	2754
DMASP-Br	i.s.	i.s.	4035	4450	3840	i.s.

[a)] i.s.: insoluble.

A detailed photophysical study of some of these fluorescent probes was presented in a previous publication.[18] Table 2 shows the absorption maxima and fluorescence emission characteristics of the synthesised fluorescent probes together with those of the commercial ones in different solvents. Solvatochromic shifts are observed for stilbene derivatives, DMANS, 2OHDEANS and DMANBu, whereas the rest of the probes are not useful to monitor polarity changes due to the lower shifts compared to those or to the lack of solubility in non-polar environments.

With regard to the aims of this paper, a wide range of excitation wavelengths (400–570 nm) can be chosen by selecting the appropriate fluorescent probe to overcome the overlap between the fluorescence emissions of the adhesive and the probe. In that sense, wide Stokes shifts as these fluorescent probes show are also desirable (Table 3). The highest Stokes shifts are observed for the diarylpolyene derivatives and the salts containing pyridinium ions (Py-1 and DMASP-Br) whereas those containing benzothiazolium ions (St-7 and DMASBT-I) show shorter Stokes shifts along with NBD-derivatives.

Fluorescence for Monitoring the UV-Curing of Acrylic Adhesives

The adhesive formulation coatings of 10 μm thickness were photocured and fluorescence changes were recorded simultaneously in real time. As can be seen in Figure 6, the spectrum of pyridine-1 in the reactive formulation L350 changes its shape with irradiation time due to an increase of the fluorescence emission and a blue shift of the maximum wavelength during UV-curing of the acrylic adhesive. This general behaviour was found in all the studied formulations with the exception of NBD amino derivatives where no peak shift was observed upon

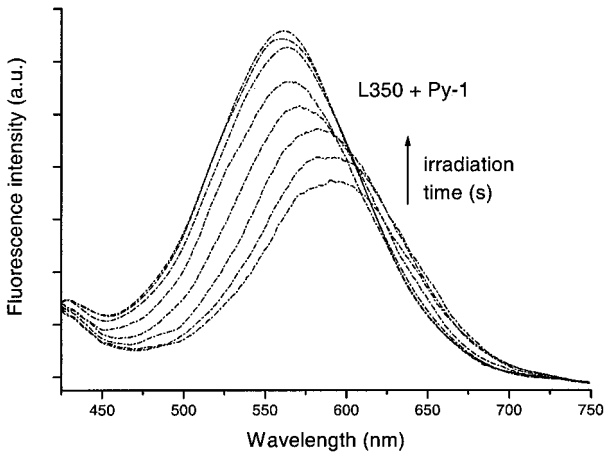


Figure 6. Fluorescence spectra of pyridine-1 at different irradiation times (every 5 s) during UV-curing of L350.

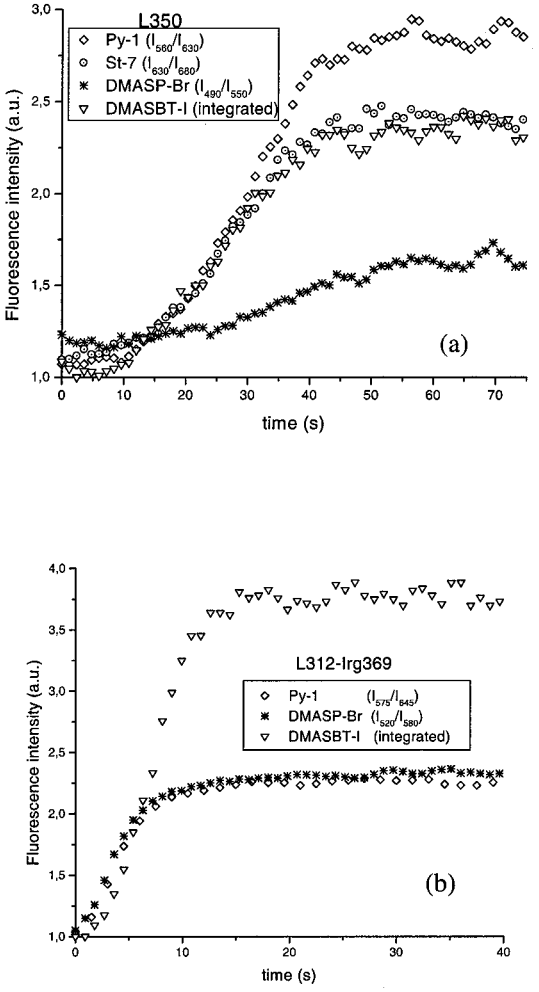


Figure 7. Fluorescence kinetics profiles of UV-curing with polychromatic continuous light of L350 (a) and L312 (b). The wavelengths selected to calculate the intensity ratio are shown in the legends for each probe.

polymerisation. Compared to the rest of the probes, this feature makes them very interesting for monitoring UV-curing since the measurements can be done following fluorescence changes at the maximum wavelength. The ratio method (intensity ratio at two different wavelengths), proposed by other authors,[25] is not useful in this case and an internal standard must be used to be independent of experimental conditions such as intensity of excitation light or fluorescent probe concentration.

Different fluorescence parameters were chosen to better describe the variations in emission: the integrated fluorescence intensity, the maximum wavelength shift and the intensity ratio at two wavelengths of the emission band. The criteria used to select these wavelengths were: the lowest one at the maximum of the spectrum of the cured sample and the highest at the half-width height of this emission band.

The changes in fluorescence of the salt probes versus irradiation time are plotted in Figures 7a and 7b for L350 and L312, respectively. The curves show the same feature as those obtained by RTIR, in some cases an induction period is observed followed by a rapid stage and then a slow period due to vitrification.

Table 4. Fluorescence rates, ρ, of the photopolymerisation of L350 and L312-Irg369 calculated by the fluorescence method along with the sensitivity of the fluorescent probes for a given adhesive formulation. The sensitivity was calculated from the slopes of the non-normalised curves of fluorescence versus the irradiation time.

Probe	L350		L312-Irg369	
	ρ	Sensitivity	ρ	Sensitivity
DMANS	0.05	0.10	0.11	0.31
DMANBu	0.04	0.06	–	–
2OHDEANS	–	–	0.11	0.31
NBD- NEt_2	0.04	0.14	0.09	0.22
NBD-NEtOH	0.04	0.06	0.11	0.17
NBD-Acr	0.05	0.09	0.12	0.18
Py-1	0.04	0.06	0.10	0.15
St-7	0.03	0.04	–	–
DMASP-Br	0.03	0.008	0.09	0.16
DMASBT-I	0.04	0.04	0.10	0.31

From the corresponding plots, the slopes, ρ, of the linear part of the normalised curves were calculated. These are proportional to the polymerisation rates and hereafter in the text, they will be called fluorescence rates. The curves for each adhesive formulation using a series of fluorescent probes were normalised between 0 and 1 to avoid the difference of the probe sensitivities and assuming the same final conversion for an adhesive formulation independently of the probe. The reliability of this assumption was confirmed by FTIR analysis as mentioned previously. The data are collected in Table 4, together with the sensitivity of the probe for a given formulation. The sensitivity was calculated from the slopes of the plots of fluorescence as a function of the irradiation time (non-normalised curves).

The values of the fluorescence rates, ρ, are similarly independent of the fluorescent probe only in the case of the less sensitive probes, lower values are found. The polymerisation rate of L312-Irg369 is double that of L350 as it was shown in the RTIR kinetic profiles. Therefore, the fluorescence rate method is useful to comparatively study series of UV-curable formulations. The sensitivity of the probe for monitoring the UV-curing process depends on the formulation. In general, fluorescence changes are broader during UV-curing of L312-Irg369 than those of L350 and this fact was interpreted as a result of the lower rigidity of the L350 polymer. In this sense, the glass transition temperatures of both UV-cured polymers were determined by DMA, showing a loss angle peak at 62 °C for L350 lower than that of L312 at 70 °C. It should be noted that the limiting conversion attained at the same curing temperature for L312-Irg369 is lower

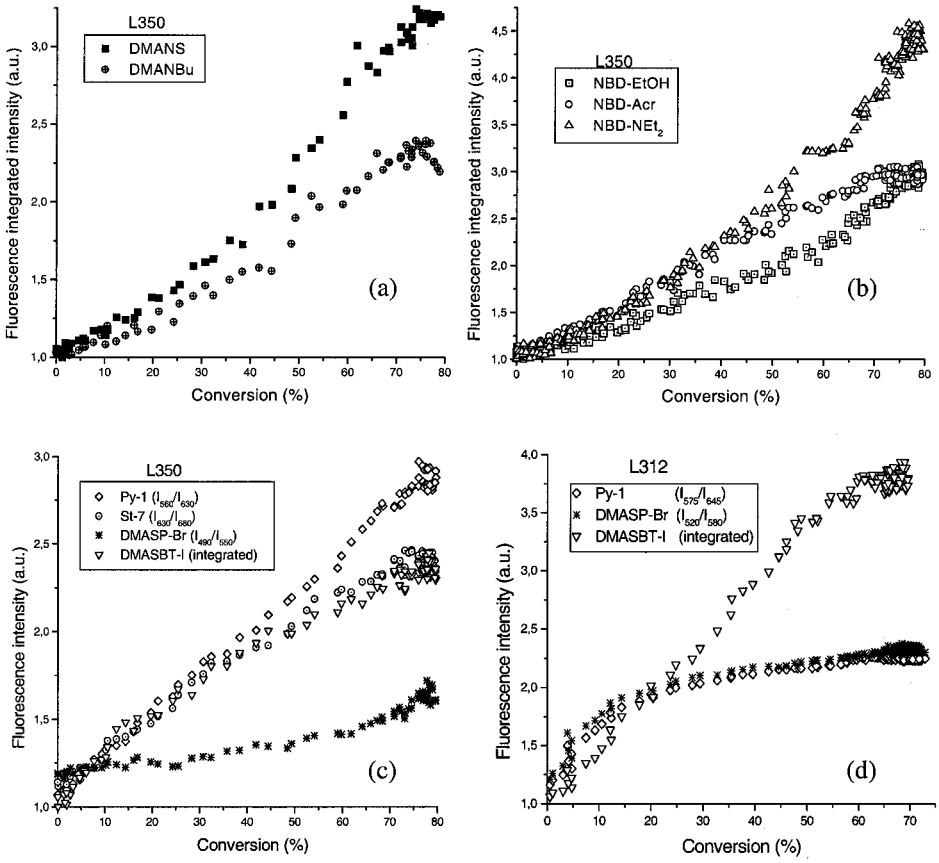


Figure 8. Plot of fluorescence changes versus conversion during UV-curing with polychromatic continuous light. (a) L350 and fluorescent probes (FP): diarylpolyene derivatives; (b) L350 and FP: NBD-derivatives; (c) L350 and FP: commercial salts and (d) L312 and FP: salts.

than for L350. In any case, the glass transition temperature for both polymers after curing is well above curing temperature. Moreover, a trend is observed between the size of the probe and the ability to sense the UV-curing process. In the case of L350, the sensitivity decreases by increasing the molecular volume of the probe:

$$NBD\text{-}NEt_2 > DMANS > NBD\text{-}Acr > DMANBu > Py1$$

$$> St7 \cong DMASBT\text{-}I \gg DMASP\text{-}Br$$

However, in L312 the sensitivity differences are less pronounced and it has been observed that the biggest probes, such as Py1 and DMASP-Br seem to be excluded from the polymeric matrix because they are not able to sense any fluorescence change after 10% conversion (Figure 8d). In L350 the highest sensitivity is shown by 4-*N,N*-diethylamino-7-nitrobenz-2-oxa-1,3-diazole, NBD-NEt_2, and thus, it can compete with DMANS which is commercially used to monitor polymerisations.[26] Otherwise, this behaviour is not general and every polymer-probe system has to be evaluated to design the best performance.

Plots of the integrated fluorescence intensity and fluorescence ratio versus conversion are shown in Figure 8a–d. Almost linear correlations between integrated fluorescence and conversion are observed during the whole polymerisation for almost all of the fluorescent probes, such as 2-[4-(dimethylamino)styryl]-1-3-ethylbenzothiazolium iodide (DMASBT-I). However, a detailed inspection shows that the general trend reflects three stages:

1. The initial stage corresponds to the rapid one observed by RTIR where the polymerisation rate increases linearly with the irradiation time. During this period, the selected fluorescence parameter also changes linearly with conversion as the photopolymerisation proceeds.
2. At about 30% conversion (Figure 8a and 8b) a change in the trend is observed in coincidence with the inflection point observed in the conversion-time curves (Figure 5) for L350. This point is typically attributed to the onset of the auto-acceleration or gel effect in bulk polymerisation processes.[27] In the case of L312 the inflection point coincides at about 10% conversion in both curves, fluorescence (Figure 8d) and RTIR.

3. In the case of NBD-NEt_2, the integrated fluorescence intensity increases at the end of the polymerisation process; the same behaviour seems to be observed for the fluorescence ratio of DMASP-Br. Therefore, for some probes it is observed that fluorescence continues increasing after limiting conversion is achieved although no further conversion is detected by FTIR. This behaviour is not general and depends on the probe-adhesive system. This suggests that the fluorescent probe response depends on the size of the probe and on the free volume of the polymeric matrix, as has been pointed out earlier.

In Figure 8b the integrated fluorescence intensity of NBD-NEt_2 increases after the limiting conversion, 80%, is attained for L350. The extension of cure was monitored by FTIR as the disappearance of the double bonds and Figure 5 shows that the maximum degree of cure is achieved after 1 minute of UV-light exposure. Therefore, although RTIR spectroscopy monitors the conversion due to the disappearance of double bonds and it is not sensitive to the very small variations in conversion occurring at long curing times after the onset of vitrification. Hence, prolonged UV-curing was found to induce modifications of fluorescence of the extrinsic probes even at high double bond conversions when limiting conversion seems to be attained. This effect was attributed to slow post-reactions that should lead to an increase in the T_g of the adhesive. To confirm this hypothesis, dynamic mechanical measurements were carried out. Figure 9 shows the dynamic mechanical spectra of the UV-cured adhesive L350 at three different irradiation times when formulation is (a) under-cured (40 s), (b) cured (1 min) and (c) post-cured (4 min). For cured and post-cured samples, the presence of a unique peak in the loss factor curve as a function of temperature seems to indicate the homogeneity of the urethane acrylate system and was attributed to the relaxation of polyacrylate chains. The maximum of the loss factor can be assigned to the glass transition temperature, being 62 °C for the cured specimen. This peak is shifted to higher temperatures (67 °C) and its magnitude decreases with longer irradiation times during UV-curing. This peak displacement shows that the glass transition temperature increases with the post-curing treatment, reflecting an increase in conversion; the lower amount of monomer and the higher molecular weights and branched structures that may appear at this stage increase the rigidity of the polymer matrix. As a consequence the probe mobility is more restricted and fluorescence intensity continues increasing. However, different behaviour is found for the reactive probe, NBD-Acr, that become covalently attached to the polymeric backbone during UV-curing and the immobilisation seems to decrease their sensitivity to these processes.

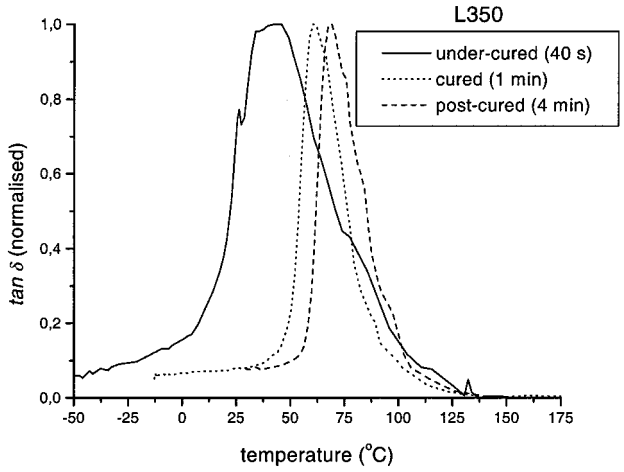


Figure 9. Dynamic mechanical spectra of L350 at different exposure times: (a) under-cured, 40 s; (b) cured, 1 min, and (c) post-cured, 4 min.

Table 5. Emission maximum wavelengths of the probes in the uncured formulations and after UV-curing.

Probe	L350		L312-Irg369	
	$\lambda_{uncured}$ nm	λ_{cured} nm	$\lambda_{uncured}$ nm	λ_{cured} nm
DMANS	554	523	550	524
DMANBu	585	532	–	–
2OHDEANS	581	523	586	554
NBD-NEt_2	485	483	–	–
NBD-NEtOH	487	487	499	499
NBD-Acr	482	481	492	492
Py-1	597	557	596	576
St-7	646	621	–	–
DMASP-Br	525	494	536	521
DMASBT-I	551	544	545	532

During UV-curing, the fluorescence maximum is blue-shifted (50–20 nm). In Table 5 the maximum wavelengths before and after UV-curing are collected. It should be noted that in the presence of NBD-derivatives, no shifts were detected during UV-curing.

Plots of the fluorescence maximum shift versus conversion are shown in Figure 10a and 10b. In general, pronounced blue shifts are observed but the mechanism causing these blue shifts should be fundamentally different.[28] For pyridine-1, a shift of 40 nm is measured during UV-curing of L350 whereas only 20 nm in the case of L312-Irg369. As has been stated before, L312 is more sensitive to vitrification than L350; as a consequence the dielectric coupling between the probe and the environment is much more inefficient for L312 than for L350 resulting in a lower blue shift. A linear correlation between λ_{max} and conversion is obtained for both polymer systems L350 and L312 with an inflection point occurring at a conversion that is coincident with the onset of autoacceleration (10% for L312 and 30% for L350). Another interesting feature appears when limiting conversion is attained,

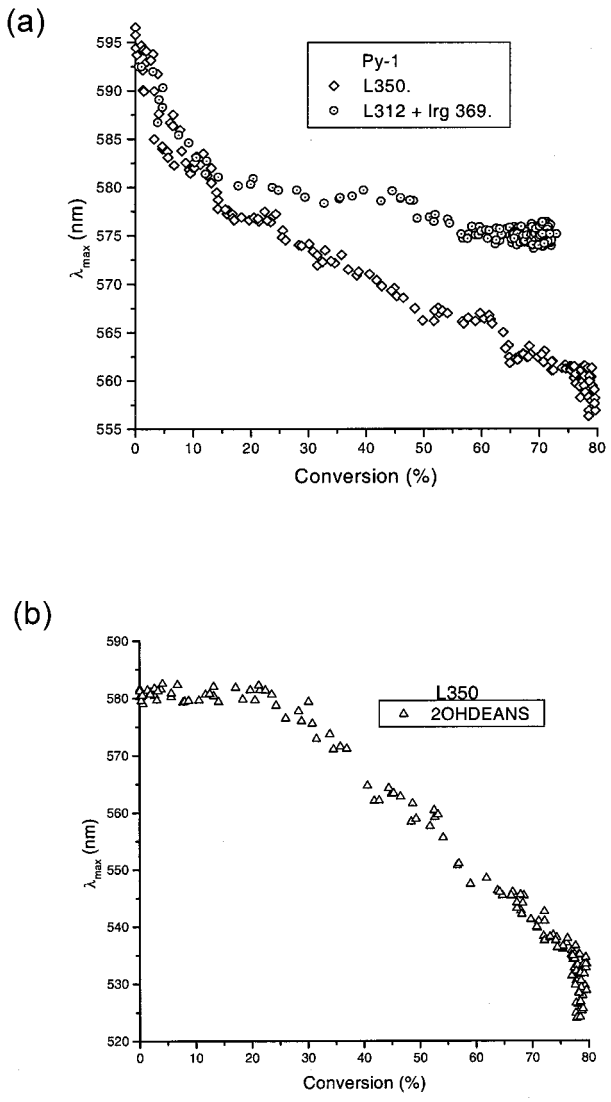


Figure 10. (a) Maximum wavelength shifts of pyridine-1 versus conversion during UV-curing of L350 (used as received) and L312 (with Irg369). (b) Maximum wavelength shifts of 2OHDEANS versus conversion during UV-curing of L350.

while a shift of the maximum wavelength operates due to the post-reactions occurring after prolonged UV-curing of L350, no shift is detected for L312. This observation is in accordance with the aforementioned higher sensitivity to vitrification of L312 in comparison with L350. The post-curing reactions of L312 are slowed down in comparison with L350 at the curing temperature; as a consequence no blue shifts are observed within the same observation time. The fluorescence maximum shift behaviour of 2OHDEANS is different in L350 although a change in the trend is observed at the same conversion (30%). The photophysical behaviour of 2OHDEANS in comparison with DMANS has been previously reported[18] and the presence of a hydroxyl group along with a pre-twisted geometry of the ground state of this molecule was related to the observed low solvatochromic effect. Preferential solvation of this fluorescent probe with methacrylic monomers by means of H-bonds provides additional stabilisation and this fact can induce less sensitivity mainly during the first stage of polymerisation. Further, the decrease of acrylic double bond concentration diminishes this effect and it is observed as a wide blue shift of fluorescence maximum (55 nm) after the first stage of the UV-curing process. This feature makes this derivative very suitable for monitoring the polymerisation of acrylic adhesives at high conversion. Moreover, a further shift of the maximum is observed when the polymerisation extent reaches the maximum value and again, this is attributed to post-reactions occurring at longer exposure times.

Further insight can be gained by a closer look at the microstructure of the polymer formed and a future paper will present a deeper study of fluorescence emission along with other properties related to the microstructure of the UV-cured adhesives.

Conclusions

We have carried out the fluorescence study of UV-curing of two different acrylic adhesives using two different photoinitiators and ten fluorescent probes. Fluorescence kinetic profiles show two stages in which linear relationships between fluorescence changes and conversion are attained but showing different slopes. The inflection point has been related to the onset of auto-acceleration. Moreover, linear correlation has been found over the whole range of polymerisation in the UV-curing of several formulations. The reactive fluorescent probe NBD-Acr becomes linked covalently to the polymer during UV-curing and then this attachment seems to be a major hindrance to the motional freedom of the probe molecule, thereby overestimating the increase of microviscosity/ rigidity imposed at the end of the reaction.

It has been observed that the fluorescence maximum wavelength is blue-shifted upon photopolymerisation and an abrupt change is observed at the irradiation time that has been related also with the onset of auto-acceleration, at which macroradicals show restricted mobility. It is well known that if the cure temperature is below the ultimate glass transition of the polymer, T_g, the system will vitrify in a conversion range that depends on the difference between the curing temperature and T_g. Once the vitrification process begins, polymerisation reactions are slowed down, the rate of which depends strongly on the rigidity of the system; for highly rigid systems like L312, no system evolution can be observed within the same observation time as for L350. In general, pronounced blue-shifts are observed upon photopolymerisation which are independent of experimental conditions. This fact makes this parameter of special use for UV-curing monitoring.

These examples illustrate the power of this technique, in which the measurement of the fluorescence intensity

and maximum wavelength shift during UV-curing of acrylics adhesives allows one to obtain information regarding to the extension of cure and thus, the quality of the product (final properties). The fluorescence method has been proved as a valuable and reliable method to comparatively study series of UV-curable adhesives.

As can be concluded from the different fluorescent probes used in this work, as well as the adhesives studied, the fluorescence method delivers good results for a wide range of formulations. Moreover, due to specific interactions between the probe and the polymer a general behaviour can not be deduced at least at this current state of knowledge. Furthermore, the use of UV-irradiation to induce curing is advantageous for heat sensitive probes and for those whose fluorescence decreases when temperature increases.

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