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CURE DEGREE ESTIMATION OF PHOTOCURABLE COATINGS BY DSC AND DIFFERENTIAL PHOTO-CALORIMETRY

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Abstract

Radiation-curable coatings have acquired importance, because they are environmentally-friendly (no solvent emission) and require low energy for curing, when compared to other conventional heat-curable products. UV-curable coatings performance depends on the cure quality. Suitable methods were evaluated to estimate the degree of cure applying quantitative techniques, such as differential scanning calorimetry (DSC) and differential photocalorimetry (DPC), in order to determine the residual heat of curing in UV-cured films. The results of the DPC technique showed better sensibility than DSC technique, although the use of suitable pans for the case of clear coats must be considered.

Keywords: photocurable materials, UV clearcoats, UV radiation curing

Introduction

Ultraviolet-radiation (UV) and electron-beam (EB) technologies of polymerization/cure have been used in a great variety of industrial applications, replacing the conventional curing process in the development of new products. This technology does not develop volatile organic compounds, has low energy consumption and high productivity, making the industrial process more efficient.

UV/EB curing technology is widely used to protect, decorate or bond items, including optic fibers, CDs/DVDs, credit cards, wood products, beverage cans, food packaging, magazine cover pages, and medical and automotive parts. The performance of the radiation-cured coatings depends on the crosslinking degree achieved during the curing process.

In this work, it was made a comparison of different methodologies to measure the degree of cure of photocurable coatings by the residual heat emanating from poly-

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merization reactions, and based on quantitative techniques of differential scanning calorimetry (DSC) and differential photocalorimetry (DPC). The technical literature brings some papers presenting DPC application to characterize the photocurable formulation; nevertheless, the results are limited and emphasize dental composites [1, 2] and wire and cable coatings [3].

DSC has been used to measure the degree of cure of some photocurable materials, but no conclusive results may be found in the technical literature. In other papers, the application of this technique to study the effect of pigment incorporation on the reactivity of printing ink formulation is also referred to. The influence of photoinitiators and UV absorbers has also been studied by DSC [4]. This paper aims to evaluate the photocurable clear coatings, which requires a change in the methodology described in the literature about the DPC.

Experimental

The coating used in this study is a basic compound formulation of 63% of Ebecryl 270 resin (aliphatic urethane diacrylate), 34% of HDODA monomer (1,6-hexanediol diacrylate), both supplied by UCB Brasil Ltd., and 3% of Darocur 1173 photoinitiator (2-hydroxy-2-methyl-1-phenyl-propane-1-one), supplied by Ciba Especialidades Químicas.

The equipment used in the cure process was LABCURA from Germetec Ultraviolet & Infrared Technology Ltd., provided with a medium-pressure mercury lamp and a variable speed belt. The ultraviolet radiation doses applied to the samples were 30, 50, 100, 200 and 600 mJ cm^{-2}. UV radiation was measured by International Light Inc.'s IL 390B Light Bug radiometer.

Enthalpy measurements were performed using Shimadzu Corporation's DSC 50 at 10°C min^{-1} heating rate from room temperature up to 250°C; and TA Instruments Thermal Analysis & Rheology's DPC 930/DSC2910 cell base, with a medium pressure lamp. DPC data were collected at 25°C, under N_2 atmosphere. Thermogravimetric measurements were performed using a TGA 50 thermobalance from Shimadzu Corporation at 20°C min^{-1} heating rate from room temperature up to 600°C.

Two different procedures were applied to prepare the samples. In the first one, 50 μm thick films were prepared on glass substrates using an automatic table and an appropriate extensor. The films were cured on LABCURA equipment in different UV radiation doses. The cured coating was removed from the glass substrate and cut in 5 mm diameter samples. The samples were put into aluminum pans, and hermetically closed using a suitable press. In the second procedure, the uncured coating was inserted into the aluminum and carbon-graphite pans. Then, the samples were cured on LABCURA in different radiation doses. DSC and DPC curves were developed with samples prepared through the application of those two different procedures. Thermogravimetric data were collected from raw materials (Ebecryl 270, HDODA and Darocur 1173) and from uncured and partially cured samples.

Results and discussion

Figure 1 shows the TG curves from raw materials, uncured coating and a film coating cured at 30 mJ cm^{-2}.

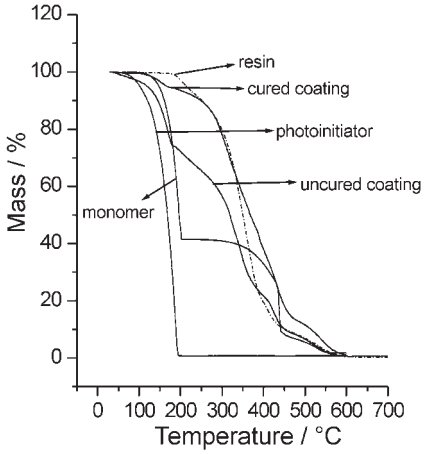

Fig. 1 TG curves from raw materials, uncured coating and coating cured at 30 mJ cm^{-2} UV radiation dose

The thermogravimetric curve of the uncured coating shows four stages of thermal decomposition. The first stage is associated to the partial volatilization of the sample components. The TG curve of the coating cured at 30 mJ cm^{-2} represents a stage of mass loss (100 to 180°C), corresponding to the photoinitiator and the monomer fraction volatilization. The sample is simultaneously submitted to the gelation and polymerization process as a heating function. This material shows thermal decomposition starting around 180°C and exhibiting thermal behavior similar to the one the resin exhibits, and different from the samples cured at higher UV doses, as it can be seen in Fig. 3. The TG curve of the photoinitiator shows only one stage of mass loss. In the monomer curve there are two steps of mass loss. The first event, between 100 and 200°C, corresponds to the partial sample volatilization; the second one, around 430°C, may be related to the thermal decomposition of the monomer polymerization product through the sample heating process. These considerations can be supported through DSC curves of the monomer. Figure 2 shows the two monomer DSC curves obtained by two different procedures. In the first one, the test was carried out in an opened aluminum pan, under nitrogen flow of 20 mL min^{-1}. Two calorimetric events in a sequence were observed. The first, endothermic, is associated to the volatilization of a sample fraction. The exothermic peak is attributed to the residual monomer fraction polymerization. In the second procedure, an aluminum pan hermetically closed was used. In the correspondent DSC curve 1 only the exothermic event can be observed, since the closed pan inhibited the sample volatilization. This exothermic peak confirms the monomer polymerization induced by heating and ob-

served visually in the residual sample after test. The peak temperature is a little different because the pressure inside the closed pan is higher than inside the opened one.

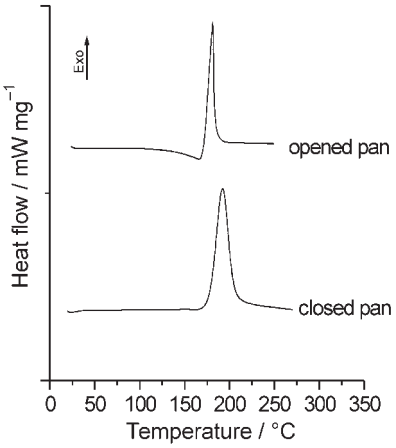

Fig. 2 Monomer DSC curves

Figure 3 shows thermogravimetric curves of uncured coating and samples cured in different radiation doses.

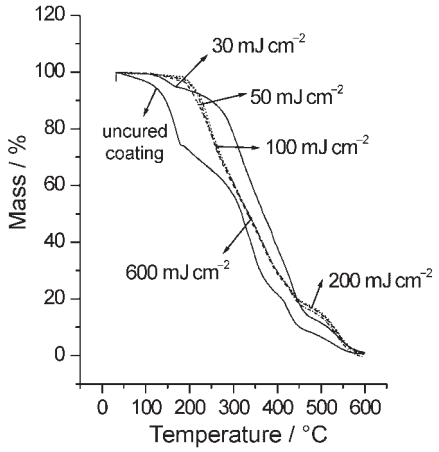

Fig. 3 TG curves from uncured coating and samples cured at different UV radiation doses

The thermogravimetric curves for samples cured in radiation doses between 50 and 600 mJ cm^{-2} exhibit a very similar behavior. The thermal decomposition of those samples occurs at a lower temperature, when compared to the curve of uncured coatings and coatings cured at 30 mJ cm^{-2}. This could indicate that the product of the self-polymerization of resin has a thermal stability higher than that of the compound formed by resin and monomer.

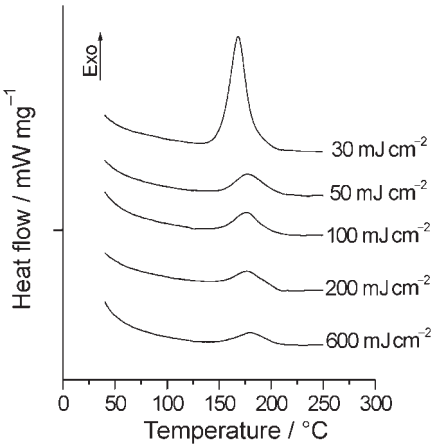

Fig. 4 DSC curves of cured samples at different UV radiation doses; aluminum pans

Figure 4 shows the DSC curves obtained from cured films transferred to aluminum pans.

In those curves, it may be observed that the exothermic peak area, concerned with the residual cure, decreases as the applied radiation is increased. The curve of the uncured coating was not shown, because its peak has a larger area when compared to the partially cured samples, which could make the observation of weak events difficult.

The degree of cure could be established by the ratio between the enthalpy peaks of partially cured samples and uncured coating.

DSC curves obtained with carbon-graphite pans show a similar behavior. The degree of cure (%) could not be established using carbon-graphite pans because of the difficulty in the enthalpy determination of the uncured coating polymerization and crosslinking. One reason is concerned with the partial volatilization of coating com-

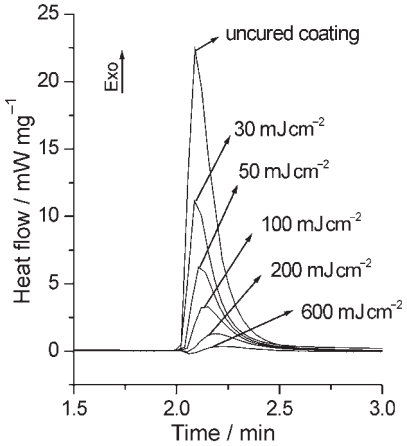

Fig. 5 DPC curves from uncured coating; and samples cured at different UV radiation doses; carbon-graphite pans

pounds, as discussed above, since the test is carried out in an open pan. The other one is concerned to the coating absorption by the porous pan, because of the long duration of the test, which polymerizes in the pan walls, making the enthalpy measurement not feasible.

Figure 5 shows the DPC curves obtained from an uncured coating and samples cured in a carbon-graphite pan. This procedure is feasible, even though there is absorption of the liquid sample by the porous pan, because the test is fast and is carried out at 25°C.

The data using aluminum pans and applying any sample preparation procedure could not be collected by DPC. The samples cured over glass substrate and transferred to the pans showed a very low thermal conductivity and an inefficient contact with the pan. Mineral oil was added to the sample to improve thermal conductivity, but it made no difference to the enthalpy measurement. The partial cure of the coating in the aluminum pan is impossible. The sample is transparent to most of the incident UV light and gets a double pass of it, because of the reflection of the pan bottom, leading to the total coating cure, irrespective of the applied radiation doses.

Table 1 shows collected data from the experiments.

Table 1 Experimental results (DSC and DPC)

Dose/ mJ cm^{-2}	DSC			DPC	
	Carbon-graphite pans	Aluminum pans		Carbon-graphite pans	
	ΔH/J g^{-1}	ΔH/J g^{-1}	Degree of cure/%	ΔH/J g^{-1}	Degree of cure/%
0	–	274.2	0.0	191.5	0.0
30	48.7	95.3	65.2	112.0	41.5
50	24.3	29.9	89.1	65.7	65.7
100	17.4	22.6	91.8	40.4	78.9
200	8.6	18.7	93.2	18.9	90.1
600	4.3	13.5	95.1	7.0	96.3

Comparing the enthalpy data of the cure of uncured coating, it may be observed that the value obtained by DSC, with aluminum hermetic pan and the sample cured as a film, is higher than the value obtained by DPC, with carbon-graphite pans.

The lower value obtained by DPC is concerned with mass loss, because of the coating absorption in the carbon-graphite pans walls during the stabilization time of the equipment, as discussed above.

The enthalpy values obtained by DSC in the partially cured samples are very close in the related curing doses between 50 and 600 mJ cm^{-2}. This demonstrates the poor sensibility of this technique regarding the poor heat transmission to the heat sensor, because of the lower thermal conductivity of the sample films and the bad contact between the sample and the pan.

The cure extent values obtained by those two techniques are very different from each other.

Conclusions

Both techniques could be applied to estimate the degree of cure of the photocurable coatings studied. In this study, DPC technique showed better sensibility when compared to DSC technique. Moreover, the operation principle of DPC equipment draws near the process used for the cure of photosensible materials. However, a pan made of a heat conductor material should be used, but it should not reflect the light, or absorb liquid samples.

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