Superior Real Time Method to Evaluate Photo-curing Resin by Means of Rigid-Body Pendulum Rheometer

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ABSTRACT: The objective of this article is to establish a new method in evaluating photo-polymerization resin reaction behavior, and to use the trends resulting from past evaluation methods and those already known to prove the feasibility of this method. Another objective is to compare the data gathered using the differential photo calorimeter (DPC) method and RPT on different photo-polymerization resin systems to illustrate that the application of RPT on photo-polymerization resin studies is more suitable. Experiment results show that the trends through the real time method using oxide series acrylate research through rigid-body Pendulum Rheometer, the photo-curing behavior under the various parameters of monomer functionality, and photo-initiator concentration can all be observed. Comparing the DPC and RPT methods on polyester acrylate series, when the oligomer of tetra-functional polyester acrylate is added with a different ratio of the monomer of propoxylated neopentyl-glycol di-acrylate, DPC evaluation methods show that the differences in observation are minimal. However, when RPT was applied, not only were the differences in reaction speed observed, but also the differences in crosslinking and other data in the hardening process when the balanced time was achieved during the oscillations procedure. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3402–3407, 2006

Key words: rigid-body pendulum rheometer; photo-curing; photo-initiator; functionality; real time

INTRODUCTION

Photo-curing resins are largely applied in semiconductor's lithography,[1] isocyanates in coating industry[2], CD protecting layer,[3] photo-curing tooth shade resin material,[4] and photo-curing adhesive.[5,6] Since photopolymers were widely applied, several literature researched on these related field. The reaction changes by means of different mixtures of the oligomer polyol, monomer, photo-initiator, and operating environment.[7] Pavlinec, Lecamp, Velankar, Kim, and Yang had adopted differential photo calorimeter (DPC)[8–12] and IR[13–21] to show the behavior of the photopolymer. Functionality content of monomer and addition of photo-initiator concentration will affect the photo-curing behavior characteristics of UV curable resin. The research of Gozzelino et al., Yilmaz et al., and Huang et al.[22–24] shows photo-resist liquid mixture of acrylic resin monomer (bisphenol-adiglycidyl-ether diacrylate) and reactive diluents monomer (tripropylene glycol diacrylate, TPGDA) and photo-initiator (2,2-dimetoxy-2-phenyl acetophenone) and its photo-curing behavior

Using the RPT,[25] the rate of photo-curing and the effect of concentration of photo-initiator to the real time of the two kinds of acrylic resin, M400 and M6210, was discussed. From the mixture of M400/M6210,[26,27] the fixed concentration of photo-initiator (I-369), when the concentration of functionality of resin monomer increases, its photosensitive nature becomes better; under energy of 150 mJ/cm^2, with more reactive functionality of M400 resin, its response speed of photo-curing is faster.

EXPERIMENTAL

Materials and sampling making

Figure 1 shows materials' chemical structure. Reactive diluents (TPGDA) and different contents of photo-initiator (2-benzyl-2-dimethylamino-1-(4-morpholino-phenyl)-butanone-1, I-369) were mixed by evenly stirring in a mixer, and then different ratios of UV curable resins (dipentaerthyol-hexa-acrylated, M400; Toagosei, Japan, and di-functional epoxy acrylate oligomer, M6210; Pufeng Industrial) were added. Polyester acrylate experiment uses the mixtures of the oligomer polyol provided by Henkel, tetra-functional polyester acrylate, model RCC-13430. The monomers used are propoxylated neopentyl-glycol diacrylate, model Photomer-4127. Photo-initiators used are from Heng Qiao, HCAP (benzoyl cyclohexanol), model Irgacure-184.

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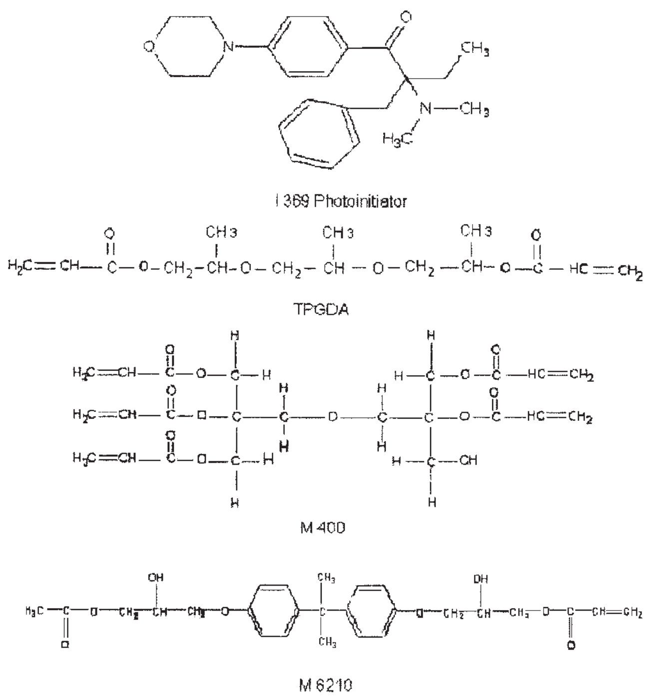

Figure 1 Chemical structure of experiment materials.

RPT measurement

This section used a rigid-body Pendulum Rheometer Model RPT-alpha 100 from Tohoku Electronic Industrial to test real time photo-curing behavior. The experiment was conducted using model RBE-160 knife-edge and frame type FRB-200 pendulum, setting the inertia at 500 g/cm; after 1 min of the experiment, the

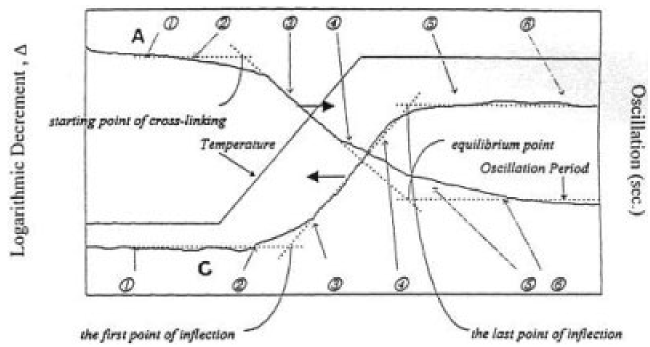

Figure 3 Typical curve of curing activity performed by rigid-body Pendulum Rheometer.

UV light was turned on and began to observe the processing of photo-curing reaction. The utilized light source was UV-L 200 UV exposure machine made by KÜHNAST. The main emission band was 365 nm and the light was beamed at 10 cm distance with 1 mW/ cm^2 illumination. Figure 2 shows the overview of this device. Figure 3 shows the illustration of classical photo-curing of rigid-body Pendulum Rheometer. The principles are illustrated as follows:

a. At curve A, the chemical bond just begins from section 2, so the oscillating cycle begins to decrease; The net slope at 3–4 indicates net bonding speed, i.e., reaction rate; while at section 6, the curve becomes more flat, which indicates that the reaction reaches a balance status.
b. At curve C, due to the fact that the reaction begins from section 2, the molecular weight increases, thus

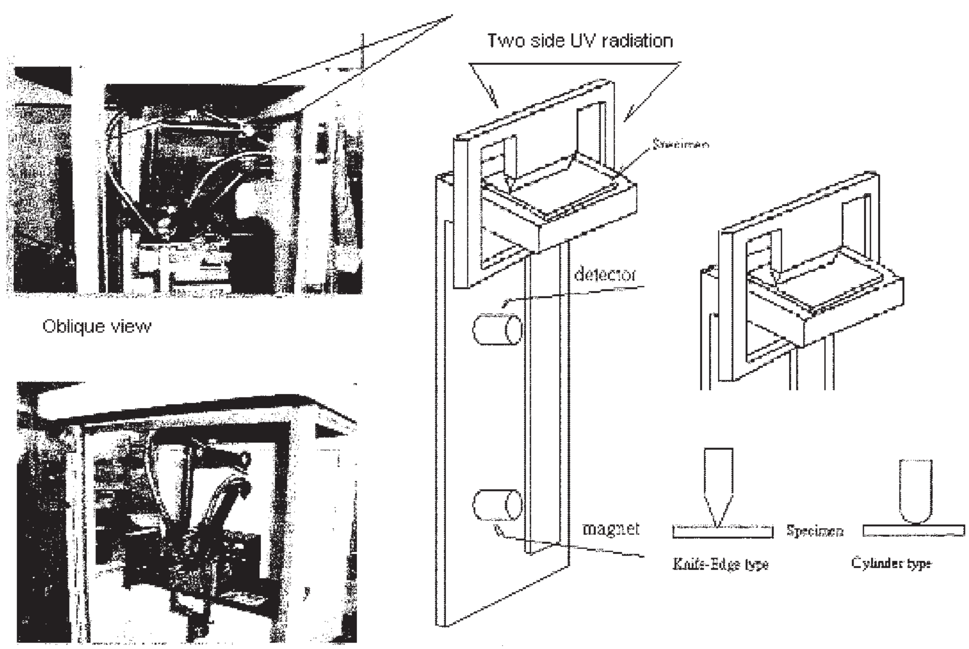

Figure 2 Sketch of rigid-body Pendulum Rheometer.

TABLE I
Formula of Various Samples

	I-369 (g)	M-400 (g)	M-6210 (g)	TPGDA (g)	RC (%)	I-369 C%
A-1	0.11	12.76	0	8.88	60	0.5
A-2	0.21	12.76	0	8.88	60	1.0
A-3	0.33	12.76	0	8.88	60	1.5
B-1	0.11	6.38	6.38	8.88	60	0.5
B-2	0.21	6.38	6.38	8.88	60	1.0
B-3	0.33	6.38	6.38	8.88	60	1.5
C-1	0.11	0	12.76	8.88	60	0.5
C-2	0.21	0	12.76	8.88	60	1.0
C-3	0.33	0	12.76	8.88	60	1.5

increasing the viscosity. Consequently, oscillating time (min) increases gradually. The increasing slope at 3–4 sections indicates an increasing speed of the viscosity. In the figure, the first point of inflection indicates gel point, so the corresponding time is the gel time. The reaction slows down after section, and the viscosity increases to infinity at this point with the curve tends to be at balance status.

DPC measurement

The DPC 930 of Du Pont tested exothermic effects. We put 10 mg sample on an aluminum plate, and placed it in an atmosphere of nitrogen at room temperature condition (25°C). The lights are turned on after 1 min of experiment, and heat flow and time graph's integral area are compared to achieve the total heat reaction. The relationship between reaction time and conversion rate was then analyzed using self-catalytic model of photo-curing dynamics software.

Self-catalytic reaction dynamics model

$$\frac{dC}{dt} = k(1 - C)^n C^m$$

where C is the conversion rate, k is the rate constant, and n and m are the reaction constants.

RESULTS AND DISCUSSION

Examination of materials of acrylic resin mixture

The photo-curing behavior is influenced by different kinds of photo-initiator materials, its content, and fixed content of resin. This material system of this experiment uses I-369 as photo-initiator, M400 and M6210 as UV curable resin, and reactive diluents as TGPDA being the resin diluting monomer.

From the experiment, it was noted that greatest solubility of photo-initiator (I-369) in diluents (TPGDA) is 1.5%; therefore, most suitable density range of I-369/TPGDA system must be less than 1.5%. This experiment selects 0.5, 1.0, and 1.5% content of photo-initiator, I-369, and uses RPT to discuss the influence of the content of photo-initiator on the photo-curing behavior.

In the related literature about crosslinking structure of photo-curing of acrylic system UV curable resin M400/M6210, Decker and Elzaouk[28] used diacrylate monomer and alkenes kind of polymer mixture system and found that the functionality of acrylic UV curable (M400/M6210) mixture with photo-initiator produces free radicals. Our research done on chemical association structure shows that its photo-curing behavior and the photo-curing association response mechanism are the same, as reported in the literature of the two scholars, Decker and Elzaouk.

Influence of photo-initiator concentration and functionality of resin on the photo-curing behavior

Rigid-body Pendulum Rheometer Tester (RPT) was used to analyze the samples indicated in Table I, which discusses the effect of content of 0.5, 1.0, 1.5% of photo-initiator on the photo-curing behavior of resin. First, samples are spread on copper sheet, forming thin film of 60 μm thickness, with a distance of 8.5 cm from ultraviolet rays, and undergo test of photo-curing real time. Figures 4–7 show the effect of change in photo-initiator concentration on photo-curing behavior of reactive diluents (TPGDA), resins (M400 and M6210), and mixture of M400/M6210 (50/50) resin, along with the increase in the concentration of photo-initiator in photo-resist liquid; speed of photo-curing increases, mean value of crosslinking density also increases. Suitable content of photo-initiator after undergoing ultraviolet radiation produces suitable amount of free radicals, giving resin a crosslinking structure, but if the concentration of photo-initiator is too much, major part of ultraviolet radiation will be easily absorbed by the surface layer of resin, hindering the crosslinking reaction in the inner layer of the spread film. Figures 4–7 show that when the concentration of photo-initiator is above 1%, there is no visible increase on the photo-curing speed of resin. Figure 4 shows

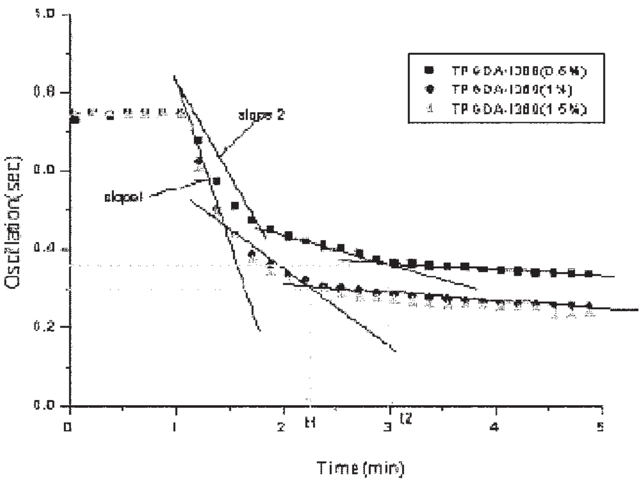

Figure 4 RPT diagram of TPGDA within various photo-initiator concentrations.

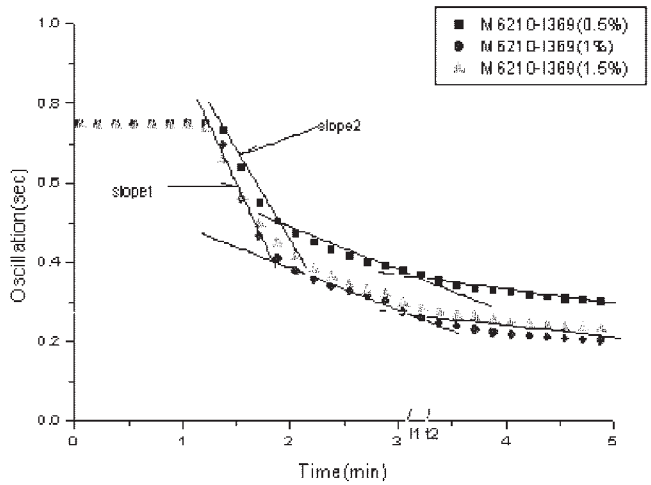

Figure 6 RPT diagram of M6210 UV curable resin within various photo-initiator concentrations.

photo-curing speed of TPGDA with different concentrations of photo-initiator. Slope 1 is the UV curing reaction rate when TPGDA is below 1 and 1.5% photo-initiator concentration. Slope 2 is the photo-curing reaction rate when TPGDA is below 0.5% photo-initiator concentration. t1 is the end point of photo-curing reaction rate when TPGDA is below 1 and 1.5% photo-initiator concentration and t2 is the end point of photo-curing reaction rate when TPGDA is below 0.5% photo-initiator concentration. Slope 1 represents photo-curing speed at 1 and 1.5% photo-initiator concentration and slope 2 represents photo-curing speed at 0.5% photo-initiator concentration; it could be observed and known that photo-curing reaction speed at 1 and 1.5% photo-initiator is faster than that of 0.5% photo-initiator content, and the photo-curing reaction termination time is shorter too. In M400 resin photo-curing behavior (Fig. 5), along with the increase in the concentration of photo-initiator, when speed of photo-curing increases, reaction termination time becomes short. Figure 7 shows the photo-curing behavior of M400/M6210 (50/50) mixture. Similarly, it has obvious response phenomenon. Although the photo-curing reaction becomes faster along with the increase in concentration of photo-initiator, once the concentration of photo-initiator reaches an extent of quantity, its speed of photo-curing will go in a definite value, and there will not be visible increase along with the increase in the concentration of photo-initiator. From the proportion comparison done in the experiment, the acrylic photo-resist liquid system with 1% photo-initiator has best result in influencing photo-curing behavior.

On the other hand, Figures 8–10 discuss the influence on the photo-curing behavior with the function-

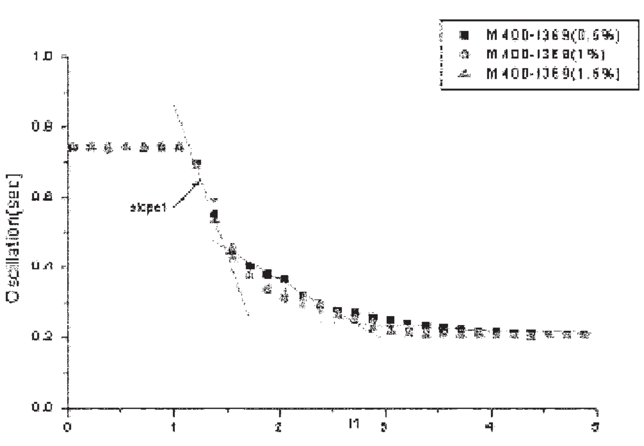

Figure 5 RPT diagram of M400 UV curable resin within various photo-initiator concentrations.

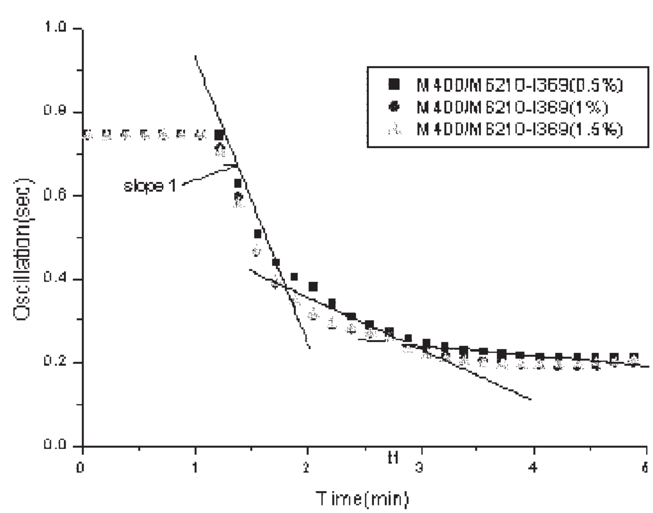

Figure 7 RPT diagram of UV curable resin M400/M6210 mixed at equal portion within various photo-initiator concentrations.

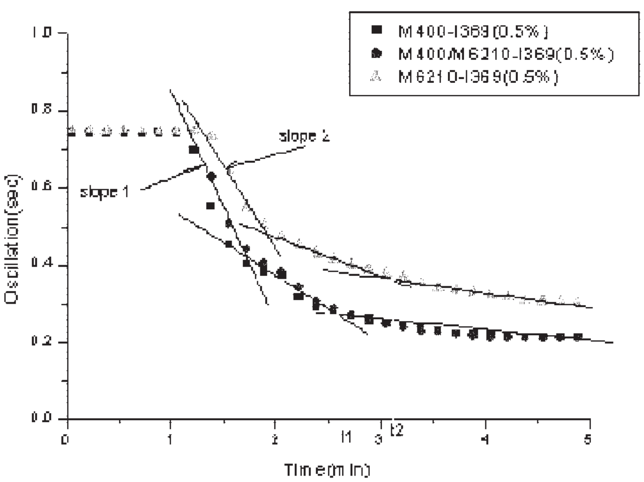

Figure 8 RPT diagram of UV curable resin M400, M6210, M400/M6210 (1:1) versus fixed 0.5% of photo-initiator.

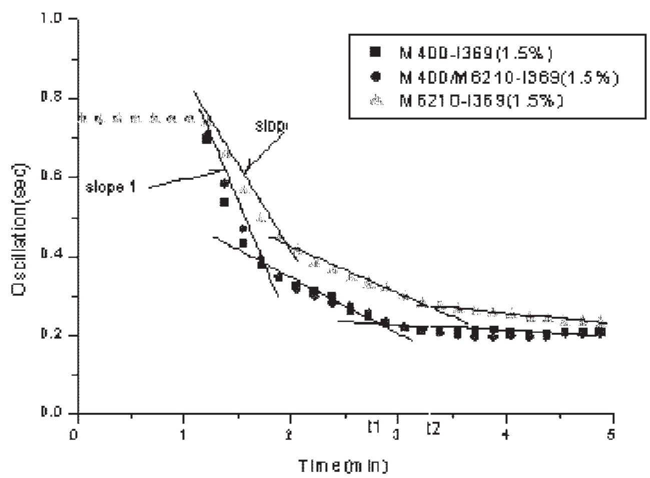

Figure 10 RPT diagram of curable resin with fixed 1.5% photo-initiator.

ality of resin at fixed concentration of photo-initiator. From the material basic structure, it can be known that M400 is a hexa-acrylated resin and M6210 resin is a di-functional base. Figure 8 shows at 0.5% photo-initiator, M400 resin and M400/M6210 (50/50) resin mixture photo-curing reaction speed slope1 is the photo-curing reaction rate when M400 and M400/M6210 is below 0.5% photo-initiator concentration, slope 2 is the photo-curing reaction rate when M6210 is below 0.5% photo-initiator concentration, t_1 is the end point of photo-curing reaction rate when M400 and M400/M6210 is below 0.5% photo-initiator concentration, t2 is the end point of photo-curing reaction rate when M6210 is below 0.5% photo-initiator concentration. (slope 1) is faster than M6210 resin reaction speed (slope 2), termination of photo-curing is comparatively shorter, and crosslinking reaction is better. Figure 9 shows at 1% fixed content of photo-initiator, slope 1 is the photo-curing reaction rate when M400 and M400/M6210 is under 1.0% concentration of photo-initiator, slope 2 is the photo-curing reaction rate when M6210 is under 1.0% photo-initiator concentration, t1 is the end point of photo-curing reaction rate when M400 and M400/M6210 is under 1.0% photo-initiator concentration, t2 is the end point of photo-curing reaction rate when M6210 is under 1.0% photo-initiator concentration, the photo-curing reaction speed of M400 resin and M400/M6210 resin mixture is better than photo-curing reaction speed and crosslinking density of M6210 resin. Similarly, at 1.5% fixed content of photo-initiator, the speed of photo-curing reaction of M400 and M400/6210 resin mixture has a better trend than the photo-curing reaction speed of M6210, reaction termination time is comparatively

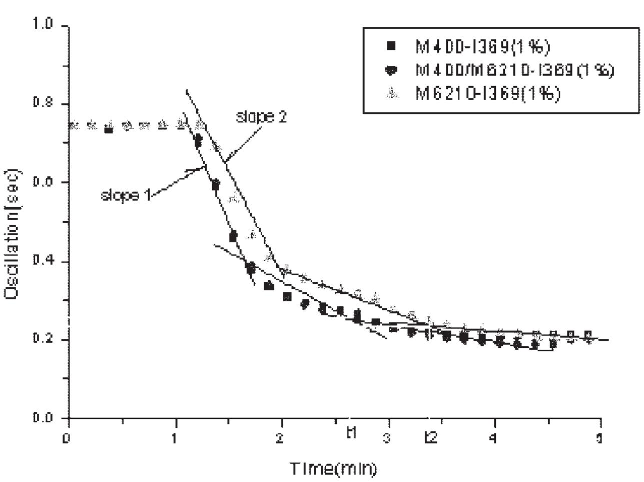

Figure 9 RPT diagram of UV curable resin with fixed 1.0% photo-initiator.

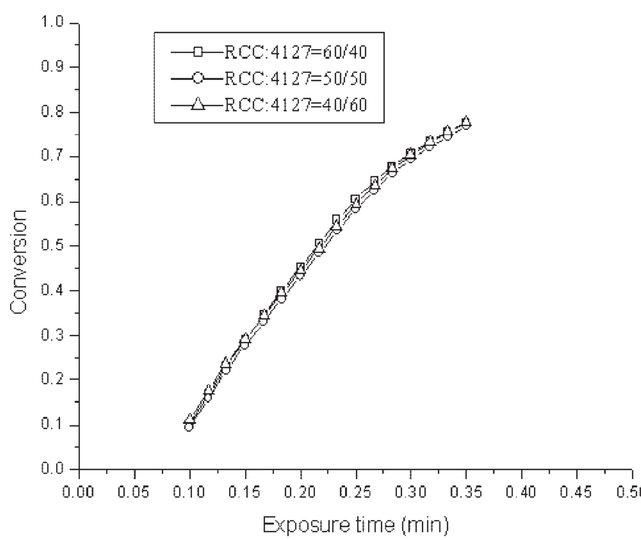

Figure 11 Conversion rate composed of different blending ratios of RCC + 4217 by DPC.

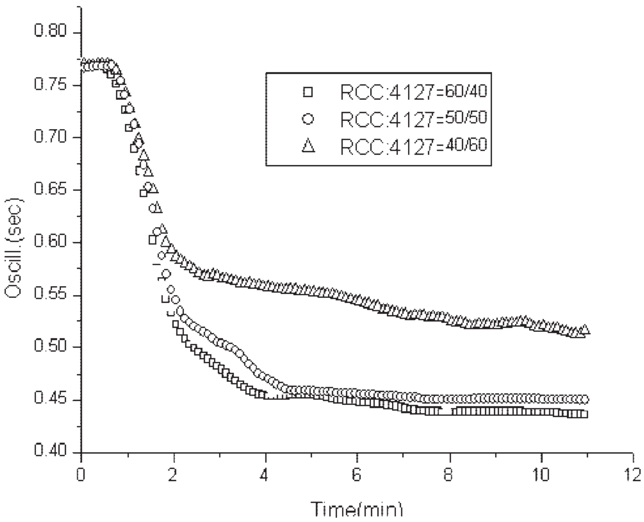

Figure 12 RPT diagram concentration effects of oscillating cycle composed of RCC + 4217.

shorter, as shown in Figure 10. Therefore, it could be clearly noted, along with increase in the functionality, under same environment and same concentration of photo-initiator the more functionality increasing collision of free radical, thus beneficial to the elevation of photo-curing speed. Therefore, it could be concluded that functionality do affect the photo-curing behavior.

Figure 11 shows the conversion rate composed of different blending ratios of RCC + 4127 test by DPC method, on the other hand, Figure 12 shows the same formula test by RPT method. This result is also caused by the different operating principles of the devices. In rigid-body Pendulum Rheometer, the waving pendulum can make the resin flow around, causing significant changes in the result, as observed in the experiment.

CONCLUSIONS

1. Concentration of photo-initiator and reactive functionality of monomer affecting the epoxy acrylate photo-curing behavior has been investigated by RPT method. This method has confirmed that trends of photo-curing behavior are not sufficiently different from previous evaluation of well-known methods.
2. Comparing the DPC and RPT methods on polyester acrylate series, we found that differences in observation were minimal in the DPC evaluation methods. With RPT, not only were different reaction speeds observed with various blending ratios, but there were also differences in resin crosslinking and oscillation time when the reactions reached equilibrium.
3. By RPT real time evaluation methods can effectively apprehend resin reaction to avoid the parameter hypothesis simulation method confusion, which resulted by DPC method.

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