Study of Oxygen Inhibition Effect on Radiation Curing

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Abstract Michael addition reaction product was used in the research of oxygen inhibition effect of radiation curing. The experimental results was measured by the content of gel and percentage of double bonds. It was proved that 9% of Michael addition product could speed up 1.2 times of the radiation curing rate at 30 kGy of EB irradiation. This kind of formulation can withstand oxygen inhibition effect obviously, so it was the foundation of application for radiation curing in atmospheric condition.

Keywords Radiation Curing Oxygen inhibition Michael addition reaction

1. Introduction

In radiation curing research, oxygen inhibition effect is an important topic, and its aim is to develop a coating formulation which could be withstood the oxygen inhibition effect and realized in atmospheric condition. If the coating research could be successful, radiation curing might be promoted with improved properties and lower investment.

In this work, we tried to search for the possibility of withstanding oxygen inhibition effect and its corresponding kinetics by using Michael reaction product in radiation cruing technology[1]. It is a foundation to develop the formulation of radiation curing under atmospheric condition.

2. Experiment

The product was synthesized by using Michael addition reaction and the urethane acrylates was also synthesized as in reference[2]. The main component of

paint included urethane acrylate, Michael reaction product and some active diluent. Four samples, with number of A_1, A_2, A_3, A_4, were prepared. In order to compare with above samples, sample B was prepared without Michael reaction product. The irradition facility used, was a set of 600 Kev Electron Accelerator of China Sichuan University. Aftre irradiation, the gel content was measured, and the double bonds percentage was determined by a set of Nicolet 20 BxS, infrared spectrometry (IR). And assuming the double bonds percentage of non-irradiated sample is 100% (standard example).

3. Results and Discussion

The gel content, double bonds percentage and its experimental condtions are listed in Table 1.

Table 1: Gel Content and Double Bonds Percentage of Different Sample*

Samples	Content of Michael Reaction Product (%)	Irradiation Dose (kGy)	Gel Content (%)	Double Bonds Percentage (%)	Double Bonds Transfer Percentage (%)
Standard example	0	0	0	100	0
B	0	30	60.1	87.3	10.7
A_1	9	10	58.7	89.9	10.1
A_2	9	20	70.9	78.7	21.3
A_3	9	30	75.8	67.2	32.8
A_4	9	40	78.5	51.9	48.1

* The irradiaton dose rate was 1 kGy $\cdot$ s^{-1}

From Table 1: the irradiation dose of sample B and sample A_3 were 30 kGy for both, however the gel content of A_3 was 75.8% and double bonds transfer percentage was 32.8% respectively, all of the results were higher than sample B without Michael reaction product. The gel content of sample B was 60.1% and double bonds transfer percentage was 12.7% respectively. It is obvious that the Michal reaction product can withstand oxygen inhibition effect in raditation curing process. To assume curing rate as R[3], then

$$R=\frac{dg}{dt}=kM(1+g)(1-g)D \qquad (1)$$

Where g is the gel content, t is the time, D is the irradiation dose, k is the

rate constant and M is regarded as the percentage of double bonds. Then the rate constant of A and B can be expressed as

$$\frac{k_A}{k_B}=\frac{M_B(1+g_B)(1-g_B)}{M_A(1+g_A)(1-g_A)}\cdot\frac{R_A}{R_B}=2.2 \qquad (2)$$

From (2), We can know that the radiation curing rate of sample A_3 is 2.2 times as big as sample B. According to Decker etal[4], the mechanism of oxygen inhibition effect can be expressed as

Chain initiated $R \xrightarrow{EB\ or\ h\nu} \dot{R} \xrightarrow{M} \dot{P}$ Chain propagated

$\dot{R} \xrightarrow{O_2} RO_2$

So that, the radiation curing process can be continued in air, it must obey the following prerequisite conditions that the eliminating rate of resolved oxygen in coating must be as fast as possible than the oxygen diffusing into coating from air, then the chain propagating can be maintained.

4. Conclusion

From this work, it is proved that the Michael addition reaction product can promote the radiation curing reaction under atmospheric condition and its effect are:

a) to speed up the radiation curing rate.

b) to play as a scavenger to eliminate oxygen resolved in coating.

Reference

[1] U. S. Patent 3,479,185.

[2] U. S. Patent 4,822,841.

[3] Ma Ive Teh and Dong Liang Chang, Radiation Phys. chem. Vol. 22, No 6 (1983).

[4] Christian Decker and Aubrey D. Terkins, Micromolecules. Vol. 18 No 6 (1985).