

Photo-DSC Studies of UV-Curable Hybrid Coating Systems

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자외선 경화형 하이브리드 코팅의 광열분석적 연구

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Abstract: UV curable hybrid systems have been investigated in the urethane acrylate based formulations where potentially irritant acrylate monomers have been substituted by vinyl ethers. Generally, among the systems studied, coating properties of hybrid system are superior to those of free radical but inferior to those of cationic systems. When the content of acrylic oligomer is above 70%, however, hybrid system could render an excellent combination of coating and curing properties which outperforms both cationic and free radical systems. Photo-DSC has been used to follow the progress of crosslinking of various coating systems. Results imply that the critical factors in determining the curing rates of coating formulations are different depending upon the formulation characteristics. In the same type of hybrid formulations, the monomer/oligomer ratio rather than photoinitiator efficiency is the critical factor determining the curing rate of the systems.

요약: 독성이 있는 아크릴 모노머를 비닐에테르로 대체시켜 우레탄아크릴레이트와 배합시키는 것을 특징으로 하는 자외선 경화형 하이브리드 시스템을 조사하였다. 일반적으로 하이브리드 시스템의 코팅 물성은 자유 라디칼계보다는 우수하나 양이온계보다는 열세하게 나타났다. 아크릴계 올리고머 함량이 70% 이상으로 배합된 경우의 하이브리드계는 코팅물성과 경화물성면에서 자유라디칼계와 양이온계보다 뛰어나게 나타났다. 다양한 코팅 시스템의 경화과정을 조사하기 위해서 광열분석기를 적용하였다. 그 결과 코팅 배합물의 경화속도에 미치는 결정적인 인자는 배합물 특성에 따라 달라짐을 알 수 있었다. 동류의 하이브리드계의 경우에는 광경화개시제의 효율보다는 모노머/올리고머 비가 더욱 중요함을 알 수 있었다.

1. Introduction

Concurrent cationic/free radical UV initiated polymerization system, due to the unique properties arising from the hybrid character, is the subject of great interest in radiation coating areas[1-6]. This is primarily related to the fact that the free radical and cationic system suffer from various drawbacks [7-8]. Where good surface cure is necessary to give a high level of scratch resistance, early curing units

of free radical system must be flashed with an inert gas to overcome oxygen inhibition. The introduction of cationic UV formulations have made nitrogen purging unnecessary for many applications. However, cationic system is susceptible to the influence of humidity and curing rate of cationic system is relatively low. Today there are many applications where the required properties can be achieved with fast line speed using the same curing facilities. Hybrid cure formulation could overcome these prob-

Table 1. Formulation Data of Various Coating Systems

System	Cationic Cat	Free RD FRI	Free RD FR2	Hybrid HD1	Hybrid HD2	Hybrid CD1	Hybrid CD2	Hybrid HD3
EB-264K		52	86	63.5		47.35	74.7	38.7
UVR-6110	86	—	—	—	—	—	—	—
EB-629	—	—	—	—	63.5	—	—	—
DVE-3	10	—	—	—	32	—	—	—
HBVE	—	—	—	32	—	47.35	20	56
HPA	—	32	—	—	—	—	—	—
TPGDA	—	10	—	—	—	—	—	—
HDDA	—	—	10	—	—	—	—	—
TMPTA	—	2	—	—	—	—	—	—
Irgacure 184	—	3	3	2.32	2.32	2.8	3.7	2.38
Irgacure 261	—	—	—	1.18	1.18	—	—	—
UVI-6974	3	—	—	—	—	1.5	0.6	1.92
BYK-307	1	1	1	1	1	1	1	1

lems. Until recently, acrylic monomer/epoxide system was used in hybrid system[9]. Due to the growing concern over the potentially carcinogenic nature of acrylic esters vinyl ethers are replacing the acrylate monomers in many formulations. Vinyl ethers[10] are excellent diluents for both acrylate and epoxy functional oligomers, thus result in low viscosity formulations. Although some of vinyl ether based hybrid systems are well established technology, the formulation scope of the hybrid system using vinyl ethers is still too narrow. In this paper, hybrid systems based on vinyl ethers have been investigated to broaden the formulation scope. Photo-DSC has been applied to follow the progress of crosslinking of various coating systems.

2. Experimental

Table 1 shows the formulation data of coating systems studied; one cationic, two free radical, and five hybrid systems. All of materials shown in Table 1 are commercially available. Triethylene glycol divinyl ether (ISP's Rapi-Cure DVE-3) and butanediol monovinyl ether (ISP's Rapi-Cure HBVE) were used as molecular diluents for hybrid system.

Hydroxypropyl acrylate (HPA), tripropylene glycol diacrylate (TPGDA), 1, 6-Hexandiol Diacrylate (HDDA), and trimethylolpropane triacrylate (TMPTA) were used as monomers for free radical system. Aliphatic urethane acrylate (UCB's EB 264K) and epoxy acrylate (UCB's EB 629) were used as oligomers. The photoinitiators used were (1-hydroxycyclohexyl) phenylmethanone (Ciba-Geigy's Irgacure 184), (2, 4-cyclopentadienyl)-(methylene)-benzene-iron(II) hexafluorophosphate (Ciba-Geigy's Irgacure 261), and triarylsulphonium salts (Cyracure's UVI-6974). The liquid formulations as shown in Table 1 were applied to the PVC substrates and the wet films were exposed to UV radiation controlled in 80W/cm of medium pressure mercury lamp.

Pencil hardness of the cured film was determined per ASTM "Standard Method for Film Hardness by Pencil Test" Method D3364-74. Crosshatch adhesion of the final film was determined per ASTM "Standard Test Method for Measuring Adhesion by Tape Test" Method D3359-83. Stain resistance was determined by applying oil ink to cured film and the seeing if the stain becomes permanent, or it can be removed by cleaning. Finally, wrinkle resistance was measured by cyclic bending the cured film on the substrate and seeing if wrinkling was introduced or not.

Photo-DSC[11-12] data were obtained by using the DuPont 930 Differential Photocalorimeter (DPC) and the DuPont 910 Differential Scanning Calorimeter. A 200 W high pressure mercury arc lamp was used in the DPC for all experiments. DuPont data analysis software was employed to generate the results from the DPC experiments. Induction time was measured from first exposure to 1 percent conversion.

3. Results and Discussion

The physical properties of the coating networks of the various types of free radical, cationic, and hybrid systems are compared in Table 2. Although

Table 2. Properties and Curing Parameters of Various Coating Systems

System	Cationic Cat	Free RD FR1	Free RD FR2	Hybrid HD1	Hybrid HD2	Hybrid CD1	Hybrid CD2	Hybrid CD3
Pencil Hardness	3H	1B	1B	HB	2H	H	2H	HB
Stain Resistance	Excellent	Bad	Bad	Good	Excellent	Bad	Excellent	Bad
Wrinkle Resistance	Bad	Good	Bad	Bad	Bad	Bad	Good	Bad
Adhesion	100	100	100	80	30	80	100	20
Induction Time(sec)	34.9	32.1	31.5	32.3	33.4	33.1	33.2	32.8
Peak Maximum (sec)	44	36	34	38	40	36	36	36
Reacted at Peak(%)	29.3	20.6	18.5	26	27.5	27.2	32.8	13.1
Enthalpy (J/g)	—	—	—	—	—	181.7	188.0	161.7
k (1/min)	5.7	12.4	12.1	8.5	8.3	11.5	13.3	4.7

uncertainties would exist due to the different formulation systems where chemistry, functionality, and initiator level are different, comparison of coating properties for the various coating systems is attempted below. Comparison of cationic system with other systems shows that cycloaliphatic epoxy/divinyl ether cationic system render an excellent combination of surface hardness, stain resistance, and adhesion properties to a cured film. The high H value of pencil hardness for the cationic system compared with their free radical and hybrid counterparts, is explained by their abstractable hydrogens overcoming oxygen inhibition at the surface of the film in the formulations. On the other hand, the improved adhesion property of cationic system is most likely related to its low shrinkage rate of the coating system. However, coating containing cycloaliphatic epoxide resulted in a brittle film leading the poor wrinkle resistance to the material. Since coatings containing cycloaliphatic epoxides tend to be brittle, other compounds must be added to improve flexibility and impact resistance. On the other hand, surface properties of hybrid system is superior to the free radical but inferior to the cationic systems. If well formulated, as with any other composite systems, hybrid system can outperforms both cationic and free radical systems and hybrid CD₂ is such an example. In an effort to have an insight for hybrid formulations, the monomer/oligomer ratio were varied in hybrid formulations. Among the

hybrid CD series, CD₂ gave rise to the hardest film and CD₃ were in the middle, and the CD₁ gave the softest film. Not surprisingly, as oligomer/monomer ratio increases, the film's hardness increases. It is due to the fact that hardness of a coating is enhanced by increasing the crosslink density of a cured film. Since the actual heat of reaction from the polymerization of the system is related to the extent of cure, the enthalpy was measured for hybrid CD series by photo-DSC and results are shown in Table 2. Data show that as enthalpy increases the coating properties improve dramatically. Since we are comparing the same formulation systems, enthalpy data appear to agree pretty well with the coating properties of the hybrid CD series such as hardness and adhesion properties.

Another factor to be considered is that the photoinitiator system used may be more suitable for one particular system than another. The effect of photoinitiator type on the coating properties showed that triarylsulphonium salts (PI 6974) appears to be better photoinitiator for HBVE/264K system than ferrocenium salts (PI 261). It may be related to the limited solubility of the ferrocenium salts in the vinyl ether systems. Furthermore, PI 261 introduced the color and this system can not be used for clear coating application. It is due to the fact that the ferrocenium salt PI 261 absorbs above 400nm and this absorption give a very strong gold color which does not completely photobleach on irradiation.

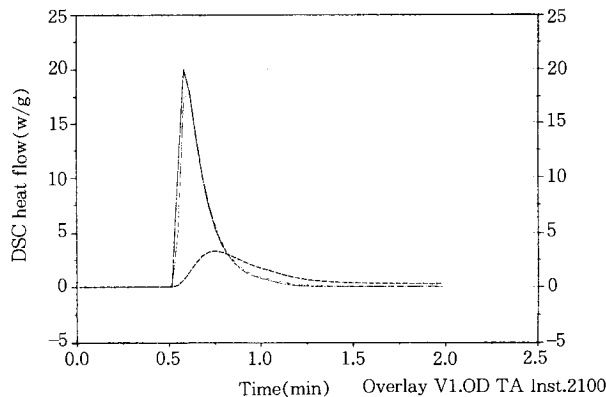


Fig. 1. Photo-DSC traces of various coating systems.

(—, Free Rd; ---, Cationic; - · - , Hybrid CD₂)

tion, introducing a brownish yellow tinge on coatings.

At this point, it is instructive to examine how these differences in formulation are reflected in the curing process. Fig. 1 presents the photo-DSC traces of coating systems studied. Traces A, B, and C are the spectra of the coatings FR₂, Cat, and CD₂, respectively. Although great care has to be exercised in interpreting results because of large variations in formulations which may effect the curing rate, comparison has been attempted again. In comparison with the peaks of free radical and hybrid systems, one observes the broad peak in the cationic systems. From the peak symmetry, induction time, and the time to peak maximum, one can get the information such as the optimum ratio of monomer to oligomer, the photoinitiator efficiency, and the reaction rate. Data of Table 2 show that system FR₂ has the shortest induction time and the shortest time to peak maximum indicating the fastest reaction system. In contrast, cationic system has the longest induction time and longest time to peak maximum suggesting the slowest reaction system. On the other hand, the induction time and the time to peak maximum of hybrid system lie between the cationic and the free radical systems. It is shown that kinetic data from the photo-DSC measurement seem to be complicated for the formulation CD series. As

the ratio of monomer/oligomer increases the induction time decreases, but the times to peak maximum does not change at all. Since the time to peak maximum indicates the point measure of the reaction velocity, this result is surprising in view of the enthalpy data. Thus, based on the above considerations, it is considered that the time to peak maximum should not be used for the kinetic analysis of the same kind of formulation systems. For the same type of formulation systems, the different approach is necessary for kinetic analysis.

In order to investigate the curing process of coating system more quantitatively, the apparent rate constant (k) was calculated by fitting of the general autocatalytic reaction model to the conversion data obtained from Photo-DSC measurement through the following equation[13-14]

$$dC/dt = kC^m(1-C)^n$$

where C is the fraction of monomer converted to polymer, k is the apparent rate constant, m is the autocatalytic reaction order, and n is the reaction order. Table 2 presents values of reaction rate constant (k) calculated from the kinetic analysis.

Again, the rate constants of cationic systems are much smaller than that of free radical system. Since high line speeds are one of the principle advantages of UV radiation curing, the slow rate is a limitation which has prevented the rapid development of widespread industrial application for UV cationic curable system, as happened with radical UV curing. Considering the rate constants and surface properties of above coating systems, one can conclude that surface curing of cationic system is faster than that of free radical system. On the other hand, cure rate comparable to the free radical polymerization of acrylate ($k=12.4$) can be achieved for the hybrid CD₂ formulation ($k=13.3$). As noted above, CD₁ is suprisingly faster curing than CD₃ in view of the qualitative analysis data of Photo-DSC measurement such as the reaction rate estimated by the time to the peak maximum. It is most likely due to the fact that as monomer content increases huge hydrogen bonding between monomers may occur

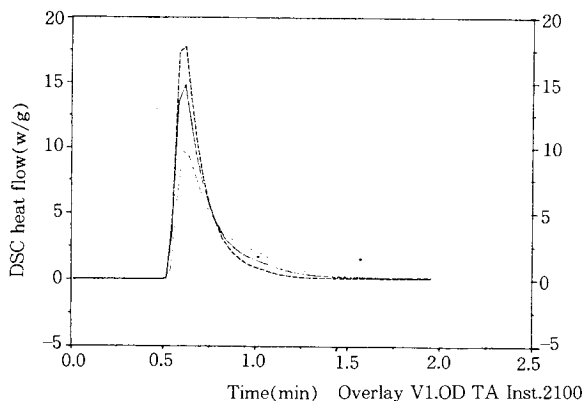


Fig. 2. Photo-DSC traces of hybrid coating systems. (—, Hybrid CD1; ···, Hybrid CD2; -·-, Hybrid CD3)

resulting high viscosity, subsequently retards the curing rate. Hybrid CD series are compared in the Fig. 2 where the peak symmetry change dramatically as the monomer content increases. This is clearly reflected in the data of the percent reacted at peak where coating CD₂ and coating CD₃ have the highest and the lowest percent values, respectively. In case of CD₃, the apparent rate constant dropped to the one third of the value obtained in the CD₂ case. Note that enthalpy data and reaction rate constant agree each other very well. Above results suggest that kinetic analysis using reaction model is more appropriate for the analysis of the same kind of formulation systems than qualitative analysis using induction time and the peak maximum data. It is also noteworthy to observe that the raw reaction rate data from the autocatalytic reaction model can provide at least a rough parameter characterizing network development during curing process regardless of the formulation types and systems.

4. Conclusions

Regardless of the formulation types, both divinyl ether/urethane acrylate and monovinyl ether/epoxy acrylate hybrid systems cure faster than free radical on the surface of the coating film without oxygen inhibition. Studied hybrid system, however, did not introduce better adhesion property than free

radical system at the film-substrate interface due to the lack of through curing. Photo-DSC was found to be a very powerful technique to investigate the various coating formulations. It was found that the kinetic analysis using reaction model and enthalpy data is more appropriate than qualitative analysis using induction time and the peak maximum data regardless of the formulation type. However, it should be mentioned that other factors such as rheological, viscoelastic, and thermal effect must be investigated further for the development of the vinyl ether based hybrid systems.

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