PAIR / P.468 / 1991

RADIATION CURING OF SURFACE COATING OF CERAMICS

Sugiarto Danu*, Anik Sunarni*,
Darsono*, and Marsongko Mitro*

KP. 270

RADIATION CURING OF SURFACE COATING OF CERAMICS

Sugiarto Danu*, Anik Sunarni*, Darsono*, and Marsongko Mitro*

ABSTRACT

RADIATION CURING OF SURFACE COATING OF CERAMICS. Electron-beam radiation curing of surface coating technology is theoritically applicable to a wide range of substrate such as wood panels, metal, ceramics, etc. In this experiment ceramics was used as a substrate. Acrylated ologomers with the trade name Laromer (epoxy-and urethane acrylate) and Aronix (oligoester acrylate) were used as coating materials after being added with reactive monomer tripropylene glycol diacrylate up to 30% by weight. Irradiation was conducted using electron-beam machine in a nitrogen atmosphere at the doses of 30, 50, and 70 kGy. The results showed that most of the films produced have a good adhesion, high hardness and excellent chemical, solvent, and stain resistances. The films prepared of urethane acrylate showed lower hardness and abrasion resistance as compared with the others.

ABSTRAK

PELAPISAN PERMUKAAN KERAMIK SECARA RADIASI. Teknologi pelapisan permukaan menggunakan radiasi berkas elektron dapat dipakai untuk bermacam-macam substrat misalnya panel kayu, logam, dan keramik. Pada percobaan ini dipakai keramik sebagai substrat. Oligomer akrilat dengan nama dagang Laromer (epoksi dan uretan akrilat) dan Aronix (oligoester akrilat) dipakai sebagai bahan pelapis setelah dicampur dengan monomer reaktif tripropilen glikol diakrilat sampai 30% berat. Iradiasi dilakukan menggunakan mesin berkas elektron dalam atmosfer nitrogen pada dosis 30, 50, dan 70 kGy. Hasil percobaan menunjukkan bahwa hampir semua lapisan yang dihasilkan mempunyai adesi yang baik, kekerasan yang tinggi, dan tahan terhadap bahan kimia, pelarut, dan stain. Lapisan yang dibuat dari iradiasi uretan akrilat mempunyai kekerasan dan ketahanan kikis lebih rendah dibanding dengan yang lain.

---

* Centre for Application of Isotopes and Radiation, NAEA

INTRODUCTION

There are many papers which review the advantages and disadvantages of radiation curing. Major advantages of the EB curing process are, a solvent free system, less energy consumption, high production rate, and processing ability at ambient temperature (1). Electron-beam machines are playing an important role in the radiation curing of coatings on a variety of substrates such as for coating of wood panels, metal, plastics, paper, and ceramics. Ceramics are widely used for construction materials, i.e. for flooring and wall covering. Conventionally, the coating process of ceramics needs 48 hours of heating at 1230°C for baking the glazed wares. Thus the energy consumption of the process is very high. Taisei Corporation and Kansai Paint Co., Ltd. Japan, have developed sucessfully a novel process for manufacturing finished gypsum tiles and marble for interior uses with EB curing of coating (2). Nakazato Ind. Japan, has produced roof tiles coated using EB curing method since 1979 (3, 4). Most of the radiation curable systems are based on molecules containing acrylate functional group and which are crosslinkable by UV or EB irradiation (5). Curing of commercial acrylate and polyester based compound with the trade name Laromer and Aronix by using UV and EB irradiation gives good physical and mechanical properties of its films.

Films cured by EB have better properties than those cured by UV (6).

This paper descripbes the EB curing of surface coating of ceramics using epoxy acrylate Laromer EA 81, urethane acrylate Laromer LR 8739, oligoester acrylate Aronic 7100 and Aronix 8060 blended with tripropylene glycol diacrylate (TPGDA).

MATERIALS AND METHODS

Materials. Uncoated ceramics from the Super Italia brand (20 x 10 x 0.8 cm) was used as substrate. Acrylated oligomer with the trade name epoxy acrylate Laromer EA 81, urethane acrylate Laromer LR 8739, and tripropylene glycol diacrylate were purchased from BASF, Germany. Oligoester acrylate Aronix 7100 and Aronix 8060 were purchased from Toagosei Chemical Industries, Co., Ltd. Japan. Those chemicals were used without further purification.

Equipments. Irradiation was carried out using an electron beam machine from Nissin-High Voltage Co., Ltd, Japan, with the maximum operation voltage and current were 300 kV and 50 mA respectively.

Methods. Coating materials were prepared by mixing the oligomers with TPGDA at various concentrations, and then coated on ceramics by using a wire bar coater to get a film thickness of around 100 μm. The wet films were exposed to electron beam radiation at various doses, i.e., 30, 50 and 70 kGy. The operation voltage was 300 kV with beam current of 30 mA. The oxygen level in the irradiation chamber was maintained at less than 500 ppm. Chemical, solvent and stain resistances, adhesion and gloss were determined according to ASTM (7,8), whereas hardness and weather resistance of the coated ceramics were measured according to JIS (9). Abrasion resistance was determined using a falling abrasive tester (natural silica sand) from a specified height through a guide tube onto the coated panel. Apparatus for falling sand abrasion test is described in the ASTM D 968 - 81. The abrasion resistance can be calculated using the following equation :

$$\text{Abrasion resistance, } \% = \frac{D - L}{D} \times 100\ \%$$

where :

D = diameter of inner tube, mm

L = length of shorter axis of abraded area, mm

RESULTS AND DISCUSSION

Viscosity is an important variable, since it will control the level of monomer needed in the coating solution to the desired application ciscosity. The oligomer - monomer ratio has a profound influence on the rate and degree of cure and ultimately on the film properties. Figure 1 shows the viscosity of various coating materials. Viscosity of the oligomers can be reduced significantly by addition of TPGDA. Without addition of TPGDA, the viscosity of oligomers used were between 4,000 and 7,000 cp. Addition with 30 % by weight of TPGDA reduced the viscosity to between 300 and 800 cp. This will be very useful in order to choose a suitable coating equipment for the coating process. At least 10 % by weight of TPGDA was needed for EA 81, Ar 7100 or Ar 8060, and 20 % TPGDA for LR 8739 to produce an even surface.

Hardness and abrasion resistance are tabulated in Table 1. Hardness and abrasion resistance were affected by irradiation dose and concentration of oligomers in coating materials. In general, these properties increase with increasing irradiation dose. This is caused by the increase of degree of crosslinking in the polimer. Addition of TPGDA as diluent to the oligomers has given different effect on the hardness. Hardness increases with the TPGDA concentration up to 30 % for Ar 7100, but no significant effect of the dilution for EA 81, LR 8739 or Ar 8060. The highest hardness was obtained in the use of Ar 8060 which gave a pencil hardness of > 6H at 50 and 70 kGy and the lowest was LR 8739 with hardness only H even at 70 kGy. Some of the results found in this experiment are in line with those reported by SENG (11), that electron-beam cured films exhibit higher hardness with increasing reactive monomers.

Figure 2 shows the histogram of adhesion between films and ceramics substrat. Almost all of the films follow the pattern that the increasing dose, decrease the adhesion. However, if the dose in too low, and degree of curing is very low, the adhesion of films must be poor. Comparing the data shown in Table 1, it seem that there is a correlation between hardness and adhesion. Comparison using the coating materials used indicates that the hardest film has the lowest adhesion grade. Laromer LR 8739 which only gives hardness H, has excellent adhesion, i.e., 5B, for all compositions and irradiation doses used. At high hardness, the film tend to become brittle and adhesion between film and substrate becomes poor.

The cured films were all resistant to the chemical and solvent used (1 % sodium carbonate, 5 % acetic acid, 10 % sulfuric acid, 50 % alcohol, 10 % sodium hydroxide, thinner) and most of them were resistant to stain (red, blue and black marker). Only films made of LR 8739 at the dose of 30 and 50 kGy were slightly affected by stain.

The weathering phenomenon of coating accurs by two general mechanisms. Those are, physical degradation and chemical transformation. Physical degradation manifest themselves as chalking, blistering, scaling and cracking. Chemical transformation is caused by chemical bonds of the material which change and lead to new physical properties. Color change, loss of gloss, and mechanical property changes are commonly associated with chemical weathering (11). Weathering data collected from this experiment and shown in Table 2 were oriented toward color change and loss of gloss. No physical degradations accurred such as chalking, blistering, scaling, peeling and cracking. In general, after 5 days of testing, the gloss loss of films made of LR 8739 was the lowest as compared with the others. The weather resistances of EA 81, Ar 7100 and Ar 8060 were nearly the same.

CONCLUSION

According to the results of the experiment as mentioned above, conclusion can be drawn as follows :

1. Films cured by EB irradiation made of epoxy acrylate Laromer EA 81, oligoester acrylate Aronix 7100 or Aronix 8060 have excellent hardness, and good chemical, solvent and stain resistances.
2. In general, high grade film hardness give an adverse effect on its adhesion, therefore the hardness of the film should be considered, in order to minimize the negative effect on adhesion.

3. Cured films, made of urethane acrylate Laromer LR 8739 have lower hardness, lower abrasion resistance, but better weather resistance than Laromer EA 81, Aronix 7100 or Aronix 8060.

ACKNOWLEDGEMENT

The authors to thank Mr. Sungkono and all operators in the EB facility for their excellent assistance in this work.

REFERENCES

1. HOLMAN, R., and OLDRING, F., UV & EB Curing Formulation for Printing Inks Coatings & Paints, SITA, London (1988).

2. MARUYAMA, T., OGAWA, M., and SUGIMOTO, K., "Electron-beam curing of surface coatings on construction materials", UNDP/IAEA/RCA Regional Executive Management Seminar On Industrial Radiation Curing Technology, Jakarta (1990), un published.

3. TABATA, Y., "Radiation curing, an overview", UNDP/IAEA/RCA Regional Executive Management Seminar On Industrial Radiation Curing Technology, Jakarta (1990), un published.

4. MURATA, K., "Electron-beam curing (EBC) of coating", Special Report for UNDP (Regional RCA Project for Asia and Pacific on Ind. Appl. of Isotopes and Rad. Tech.), UNDP-IAEA, Vienna (1980) 383.

5. SENICH, G.A., and FLORIN, R.E., Radiation curing of coatings, Rev. Macromol. Chem. Phys. C 24 2 (1984) 239.

6. DANU, S., SUNDARDI, F., TRIMULYADI, G., KICKY, L.T.K., SUNARNI, A., and DARSONO., "Radiation curing of commercial acrylate and polyester based compound for surface coating", First Indonesia-JICA Polymer Sym-

posium Cum-Workshop, 1989, RDCAP-LIPI, Bandung (1989) 160.

7. AMERICAN SOCIETY FOR TESTING AND MATERIALS, Annual Book of ASTM Standards, part 21 ASTM, Philadelphia (1972) 474.

8. AMERICAN SOCIETY FOR TESTING AND MATERIALS, Annual Book of ASTM Standards, part 27 ASTM, Philadelphia (1982) 104.

9. JAPANESE INDUSTRIAL STANDARD, Testing Methods for Organic Coatings, JIS K 5401 (1970) 72, 77.

10. SENG, H.P., Test methods for the characterisation of UV and EB cured printing varnishes, Part 2, Beta-Gamma 4 (1989) 25.

11. VAN LANDUYT, D.C., and LEYRER, S.P., Physical and electrical properties of acrylic oligomers, Radiation Curing, May (1982) 10.

Table 1. Hardness and abrasion resistance of cured films

Composition		Pencil hardness			Abrasion resistance, %		
		Dose, kGy			Dose, kGy		
		30	50	70	30	50	70
%	100	2H	3H	5H	67.5	65	72.5
EA 81	90	3H	3H	5H	62.5	70	65
in	80	3H	3H	4H	67.5	67.5	75
TPGDA	70	3H	3H	3H	70	62.5	62.5
%	100	F	F	F	47.5	55	70
LR 8739	90	H	H	H	55	52.5	60
in	80	H	H	H	50	65	57.5
TPGDA	70	H	H	H	50	57.5	57.5
%	100	3H	3H	4H	65	65	70
Ar 7100	90	4H	4H	5H	65	70	72.5
in	80	4H	4H	>6H	62.5	70	70
TPGDA	70	5H	5H	>6H	62.5	65	67.5
%	100	5H	>6H	>6H	65	72.5	70
Ar 8060	90	5H	>6H	>6H	70	65	75
in	80	5H	>6H	>6H	67.5	65	65
TPGDA	70	5H	>6H	>6H	62.5	67	65

Table 2. Accelerated weathering test of coated ceramics

Dose, kGy		30				50				70			
% EA 81 in TPGDA		100	90	80	70	100	90	80	70	100	90	80	70
Duration of testing, days	0	87	87	85	84	85	75	78	72	85	82	82	88
	5	84	81	82	81	81	65	74	65	82	73	78	86
% Loss of gloss		3.4	6.9	3.5	3.6	4.7	13.3	5.1	9.7	3.5	10.9	4.8	2.2
% Avg.loss of gl.		4.4				8.2				5.4			

Dose, kGy		30				50				70			
% LR 8739 in TPGDA		100	90	80	70	100	90	80	70	100	90	80	70
Duration of testing, days	0	80	84	78	82	84	80	80	69	80	80	79	82
	5	78	81	75	74	82	78	77	64	72	78	74	80
% Loss of gloss		2.5	3.6	3.8	9.8	2.4	2.5	3.7	7.2	10	2.5	6.3	2.4
% Avg.loss of gl.		4.9				3.9				5.3			

Dose, kGy		30				50				70			
% AR 7100 in TPGDA		100	90	80	70	100	90	80	70	100	90	80	70
Duration of testing, days	0	90	79	83	87	88	79	84	76	88	80	80	84
	5	80	74	80	81	83	66	81	70	84	72	72	80
% Loss of gloss		11.0	6.3	3.6	6.9	5.7	16.4	3.6	7.9	4.5	10	10	4.8
% Avg.loss of gl.		6.9				8.4				7.3			

Dose, kGy		30				50				70			
% AR 8060 in TPGDA		100	90	80	70	100	90	80	70	100	90	80	70
Duration of testing, days	0	84	84	87	81	86	80	88	88	82	80	78	73
	5	78	79	76	69	80	75	80	83	80	73	70	70
% Loss of gloss		7.1	6.0	12.6	14.8	7.0	6.2	9.1	5.7	2.4	8.7	10.2	4.1
% Avg.loss of gl.		10.1				7.0				6.3			

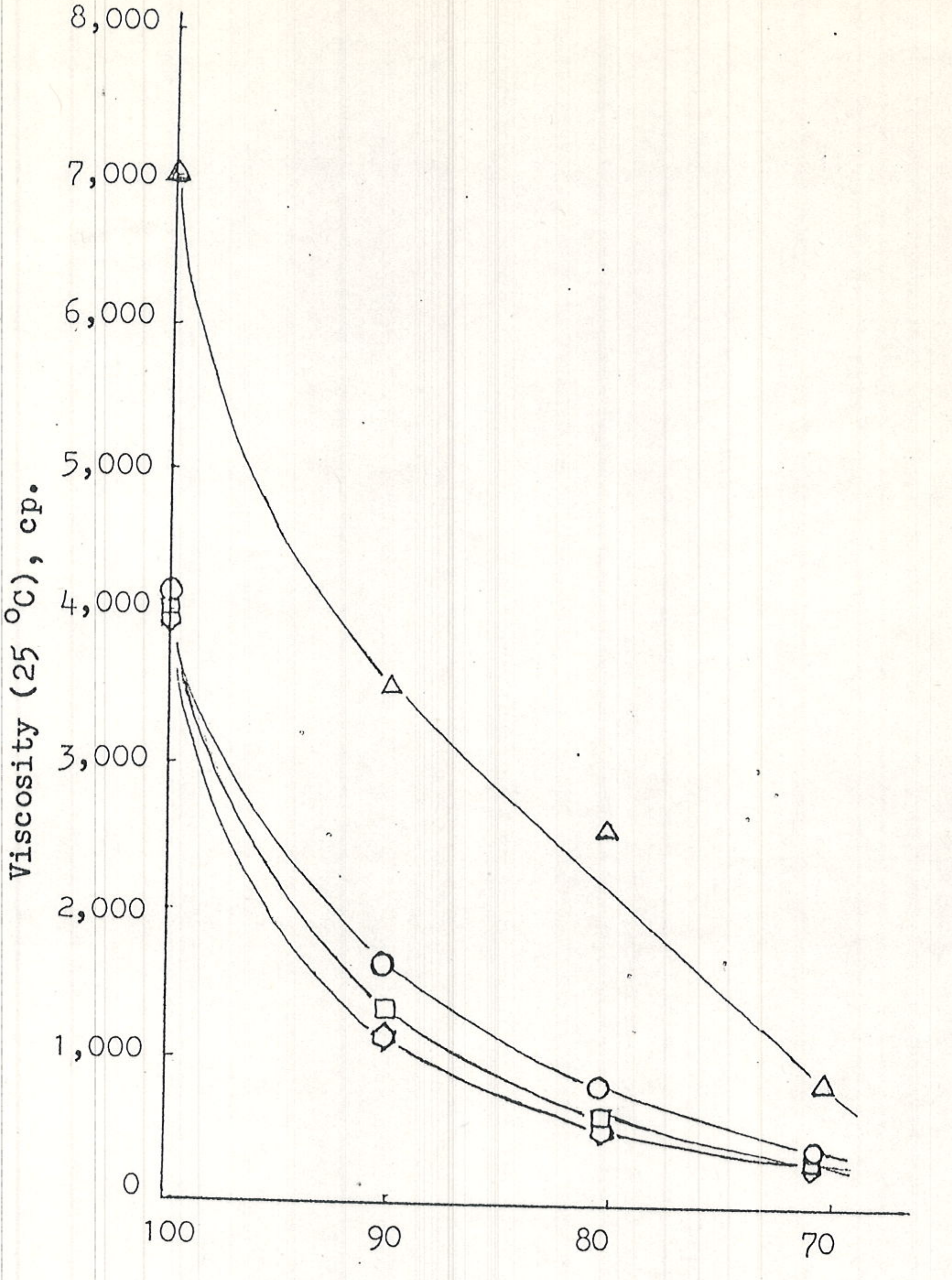

Fig 1. Viscosity of coating materials.

△ - LR 8739
○ - Ar 7100
□ - EA 81
⬡ - Ar 8060

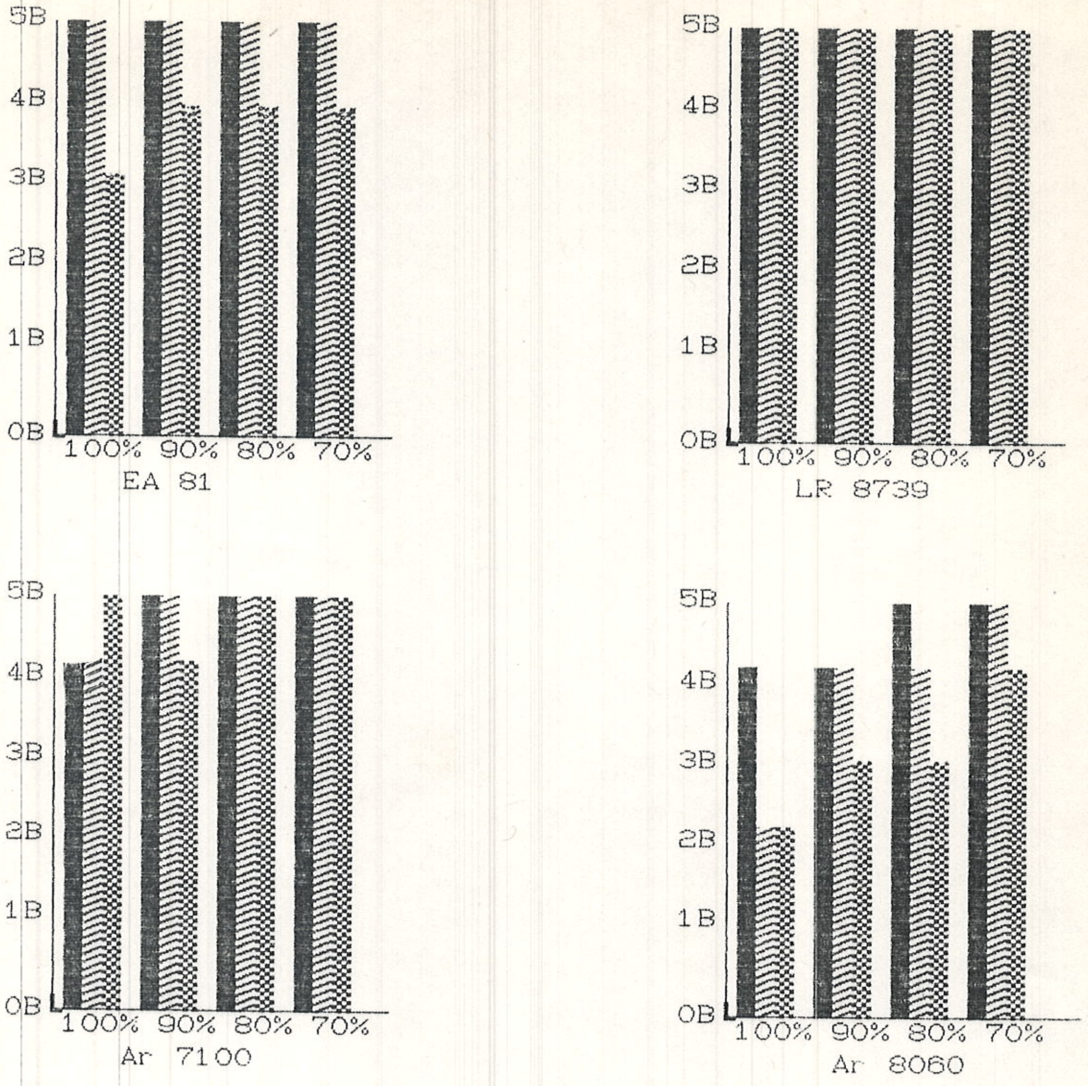

Fig. 2. Histogram of the adhesion of cured films on ceramics substrate.

Composition of coating materials are expressed in % of oligomer in TPGDA

▮ = 30 kGy ▨ = 50 kGy ▩ = 70 kGy

Note : 5B - % removal 0
4B - % removal $0<a<5$
3B - % removal $5<a<15$
2B - % removal $15<a<35$
1B - % removal $35<a<65$
0B - % removal >65