

Synthesis and Characterization of UV-curable Polyurethane Acrylates Coating Resins for PVC Tiles

Hong Zhao¹ and Jin-Wook Ha^{1*}

¹Dept. of Chemical & Environmental Eng., College of Eng., Soonchunhyang Univ.

PVC 바닥상재용 광경화형 폴리우레탄 아크릴 수지의 합성 및 특성고찰

조홍¹, 하진욱^{1*}

¹순천향대학교 화학공학환경공학과

Abstract The Application of UV curing technique for poly (vinyl chloride) (PVC) floor tiles coating has improved the quality of PVC floor. Several formulations were made including acrylated oligomers based on a polyurethane were blended with reactive monomers, photoinitiators and other additives. The used oligomers are commercial aliphatic urethane acrylates. Thin films were prepared on PVC tiles by bar coating with different formulations using UV radiation. The coating resins were characterized by FTIR. The properties of UV-cured films such as gloss and adhesion were examined. The properties of UV-cured films dependent on the influence of composition and processing conditions was studied.

요 약 광경화(UV-curing)에 의한 PVC 바닥상재 코팅기술은 PVC 바닥상재 질의 개선을 위하여 사용되는 것이다. 본 연구에서 사용한 폴리우레탄 아크릴레이트 수지는 반응성 모노머, 광개시제, 그 외 첨가제를 배합하여 제조하였고, 올리고머는 상용화된 지방족 우레탄 아크릴레이트를 사용하였다. 제조한 코팅액을 바코팅(bar-coating) 방법으로 PVC 바닥상재에 코팅한 후 광경화법을 이용하여 상재표면에 코팅층을 형성하였다. 코팅에 사용된 코팅액은 FTIR로 측정하여 특성을 확인하였으며, PVC 상재 표면에 형성된 코팅층의 물성은 광택과 부착력으로 평가하였다. 코팅층의 물성은 코팅조성과 공정조건에 영향을 받았다.

Key Words : UV-Curable Coatings; Polyurethane Acrylate; FTIR; Adhesion

1. Introduction

UV radiation curing has become a well-accepted technology which has found a large number of applications in various industrial areas such as inks, adhesive and coatings. [1] UV radiation curing involves the polymerization and cross-linking of functional monomers and oligomers (usually liquid) into a cross-linked polymer network (usually a solid film) induced by photons. [2] UV-curable formulations usually contain three basic components: photoinitiators, functionalized oligomers and monomers. [1] The great

reactivity of acrylate monomers, together with the large choice of acrylate-functionalised oligomers, have afforded these radical-systems a leading position in UV-curing applications. [3] Among the commercially acrylated oligomers, the urethane acrylate is to combine the high performance and many possible applications of polyurethane coating systems with the curing rate and efficiency of photopolymerization. [4] To comply with the needs of coatings and curing processes and to achieve the desired protective effects, the formulation of UV-curable coatings requires considerable skill in balancing a number of competing properties such as flexibility, adhesion,

*Corresponding Author : Jin-Wook Ha(chejwh@sch.ac.kr)

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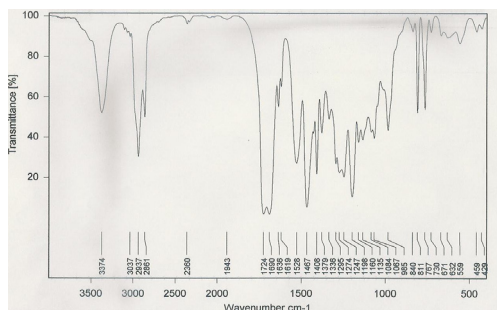
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toughness, abrasion resistance, resistance to discoloration, chemical and stain resistance, as well as cure rate. [5] The acrylated polyurethanes are recommended for abrasion resistance for PVC floor tiles.

2. Experimental

2.1. Materials

The UV curable urethane acrylate system was made up of three main components: firstly, aliphatic urethane acrylate oligomers secondly, reactive monomer and thirdly, the photoinitiators used to obtain the UV curable coatings. The FTIR spectrum of an aliphatic urethane acrylate oligomer used in this work showed in Fig. 1.



[Fig. 1] FTIR spectrum of polyurethane acrylate oligomer

The reactive diluents were monofunctional acrylate monomers and multifunctional acrylate monomers, 1-hydroxycyclohexyl-phenyl-ketone (HCPK) and benzophenone were used as photoinitiators. And the quencher (SiO₂) were used as additive.

2.2. Application

A series of two UV curing coating compositions were prepared by mixing to a uniform consistency components listed in Table 1.

In order to investigate the performance of the cured film, each UV curable coating was coated onto PVC tile using a bar coating (No. 7) and cured in a conveyer belt type UV curing system LZ-UH101RCH (Lichtzen Korea) equipped with a high-pressure mercury lamp (main wavelength: 250~420nm, velocity of conveyer belt:

1.5m/min, radiation intensity: 1.5 kW).

[Table 1] Formulations of coating resins

| Components | Compositions (wt.%) | |
|----------------|---------------------|-------------|
| | Non-glossy | Half-glossy |
| monomers | 49.1 | 50.0 |
| oligomers | 17.7 | 29.4 |
| Additives | 5.0 | 3.9 |
| diluents | 24.7 | 12.6 |
| photoinitiator | 3.5 | 4.1 |
| Total | 100 | 100 |

2.3. Laboratory tests

2.3.1 Viscosity

The viscosity of the samples was measured with a Rion viscotester (VT-03F) at 298K.

[Table 2] Viscosity of the coating formulations

| Resin | Viscosity (298K) |
|-------------|------------------|
| Non-glossy | 430 cP |
| Half-glossy | 180 cP |

2.3.2 Adhesion measurements

The adhesion measurements were carried out using the tape test method according to ASTM D 3359 standard specification. [6]

2.3.3 Gloss measurements

The gloss grade of cured film was determined at 60° using a micro-gloss (BYK, Germany).

3. Results and Discussion

3.1. Functional group analysis of resins

Because polyurethane acrylate oligomer has features of high reactivity and fine mechanical properties, we used the reactive polyurethane acrylate oligomers as coating agents. Fourier transform infrared spectroscopy is well established as an analytical technique for functional group analysis. The structure of the formulations were characterized by FTIR. FTIR spectra was taken within the

scanning range of $400\text{--}4,000\text{cm}^{-1}$ for 32 times at room temperature.

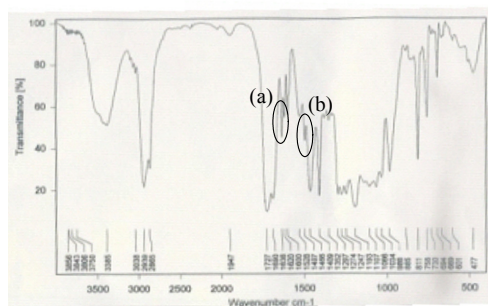
Fig. 1 shows the FTIR spectrum of one commercial aliphatic urethane acrylate oligomer used in our work. In urethane oligomer, the absorption of -NH- at 3374cm^{-1} , -CN- at 1528cm^{-1} and -COO at 1724cm^{-1} revealed the formation of urethane group. The absorption of -C=C- was at 1636cm^{-1} , 1408cm^{-1} and 811cm^{-1} . A tight cluster of bands at 2861 to 2937cm^{-1} due to its aliphatic groups. Therefore, the functional groups structure of oligomer could be confirmed.

Fig. 2 shows the FTIR spectrum of non-glossy UV-curable coating formulations. The main functional groups were the same as aliphatic urethane acrylate oligomer, but there appeared a group of bands related to aromatic content (e.g. bands at 1600 and 1497cm^{-1}).

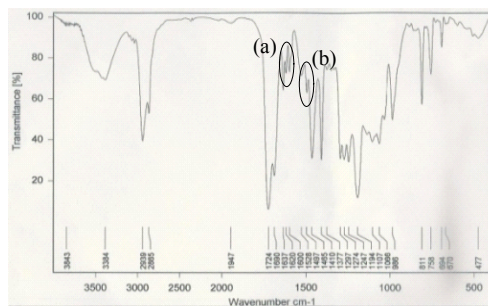
Fig. 3 shows the FTIR spectrum of half-glossy coating composition. Compared with non-glossy composition, the maximum peaks of functional groups were very similar. It was observed that the relative absorption intensity of amide bands (C-N and N-H) of urethane at 1528 and 1379cm^{-1} in Fig. 1 decreased significantly in Fig. 2 and Fig. 3.

[Table 3] Assignments of the peaks of FTIR spectrum for non-glossy formulation

| Wave No. (cm^{-1}) | Assignment |
|-------------------------------|---|
| 3385 | Stretching vibration of the urethane N-H bond |
| 2865–2939 | Stretching vibration of the aliphatic C-H bond |
| 1690–1727 | Amide I, stretching vibration of the C=O bond |
| 1600 | Stretching vibration of the benzene C-C |
| 1528 | Amide II |
| 1466 | Bending vibration of the aliphatic C-H bond [7] |
| 1409 | Stretching vibration of C-C in RCH=CH_2 |
| | Stretching vibration of the benzene C-C |
| 1247 | Amide III, antisymmetric stretching vibration of CO-O-C |
| 1107 | Symmetric stretching vibration of CO-O-C [8] |
| 1066 | Symmetric stretching vibration of CO-O-C |
| 811 | Out-of-plane bending of C-H in RCH=CH_2 |
| | Out-of-plane bending of C-H in benzene ring |



[Fig. 2] FTIR spectrum of non-glossy coating formulation; (a) Stretching vibration of the benzene C-C (1600cm^{-1}), (b) Stretching vibration of C=C bond in benzene ring (1497cm^{-1})



[Fig. 3] FTIR spectrum of half-glossy coating formulation; (a) Stretching vibration of the benzene C-C (1600cm^{-1}), (b) Stretching vibration of C=C bond in benzene ring (1497cm^{-1})

3.2. General performance of coatings

3.2.1 Consideration for photoinitiators

The selection of photoinitiators was made by the specifications the final cured coating has to fulfill, for this work we need no yellowing and clearcoat with good durability. For PVC tiles coating, key elements we have to take into consideration were the resin absorption and yellowing problem of the cured film related to photoinitiator type and concentration. So we used combination of HCPK and BP as photoinitiators. HCPK has the high reactivity in an acrylate formulation as non-yellowing photoinitiator, BP as a photoinitiator used in the photocrosslinking has some advantages, such as its cheap price, high photoinitiating efficiency. It illustrated that the efficient photoinitiator system exhibiting fast

curing rates was selected since the cured PVC tiles had clear and non-yellowing appearances.

3.2.2 Consideration for adhesion

Adhesion is considered to be of major importance when formulating surface coatings. As the major components in UV-curing systems, monomers and oligomers can be selected on the basis of their effects on adhesion. The adhesion of cured films to the substrate is influenced by a large number of parameters such as substrate wetting, absorption between film and substrate, surface swelling of substrate volume shrinkage and so on.

PVC tiles can be wetted when the surface tension of the formulation is lower than that of the substrate. The surface tension strongly depends on the polarity of the resins, which is essentially determined by the type and number of the functional groups. Polar groups, such as hydroxy or carboxy groups, increase the surface tension. So nonpolar groups such as long-chain aliphatic acrylate monomers was selected to reduce the surface tension of the formulation. Acrylate monomers can induce surface swelling of plastics such as PVC. Monomers can be used singly or in combination of two or more of them.

According to experiences and applications, PEGDA was used as a diluent to reduce the viscosity of formulations in our work. Adhesion achieved in non-glossy and half-glossy coatings reached maximum value, 5B, for PVC surface.

3.2.3 Consideration for gloss

[Table 4] Adhesion and gloss of UV-cured non-glossy coatings on PVC tiles

| | Adhesion (5B) | | |
|----------------------------|---------------|---------|----------|
| | Test I | Test II | Test III |
| Non-glossy (Gloss 60°) | 10.9 | 11.0 | 10.5 |
| Half-glossy (Gloss 60°) | 44.7 | 49.1 | 47.3 |

Table 1 shows the acrylate content of the two coating resins. Compared with about 62% of acrylate content in half-glossy coating resin, acrylate content of non-glossy formulations was more than 70%. It is observed from

Table 4 a decrease in gloss when the acrylate content increase, due to the lower content of urethane groups.

4. Conclusions

Flooring applications such as vinyl coatings continue to use UV-curable technology to a growing extent, primarily for the excellent abrasion resistance and for the quick curing rate. The UV-curable polyurethane acrylates for PVC tiles coating were formulated from aliphatic urethane acrylate oligomer, several acrylate monomers, and photoinitiators.

1-hydroxy-cyclohexyl-phenyl-ketone and benzophenone were used as photoinitiators and PEGDA was a diluent. In practice, adhesion is considered to be of major importance when formulating UV-curable coatings for PVC tiles since most other tests would assume that good adhesive power between the coating and substrate exists. In this paper the choice of oligomers and monomers was made by the adhesion requirements. The application performance of the coatings is to aim for a balance of a good adhesion and required gloss. Although the oligomer weight percents were different, which in half-glossy resin was nearly twice as that in non-glossy resin, there was no direct influence on the adhesive power of the two formulations. The adhesion both reached maximum value, 5B, and equivalent to 0% of the removed area. The selection and mixing ratios of aliphatic urethane acrylate oligomer and acrylate monomers gave the good examples and this can broaden the application of UV curable coatings further on PVC floor industry later.

참고문헌

- [1] C. Decker, "Kinetic Study and New Applications of UV Radiation Curing", *Macromol. Rapid. Commun.* Vol. 23, pp. 1067, 2002.
- [2] Nichols, M.E., Seubert, C.M., Weber, W.H., and Gerlock, J.L., "A Simple Raman Technique to Measure the Degree of Cure in UV-Curable Coatings," *Prog. Org. Coat.*, 43, pp. 226-232, 2001.
- [3] C. Decker, "Photoinitiated Crosslinking Polymerisation", *Prog. Polym. Sci.*, Vol. 21, pp. 600, 1996.

- [4] "Polyurethanes-Coatings, Adhesives and Sealants", U. Meier-Westhues, Vincentz Network, Hannover 2007.
- [5] B.H. Lee, JCT Research, Vol. 3, No. 3, July 2006.
- [6] ASTM D 3359-2002. "Standard test methods for measuring adhesion by tape test". Method B (Cross-cut tape test). Annual Book of Standards, Section 6, Vol. 06.01, 2002 (Easton, MD ASTM, 2003).
- [7] K. Nakayama, T. Ino and I. Matsubara, "Infrared Spectra and Structure of Polyurethane Elastomers from Polytetrahydrofuran, Diphenylmethane-4, 4'-diisocyanate, and Ethylenediamine", *J. Macromol. Sci-Chem.* A 3, pp.1005. 1969
- [8] Y. Zhang, R.J. Heath and D.J. Hourston, "NF-kappa B activation and the inhibitory effect of dexamethasone in experimental asthmatic guinea pigs", *J. Appl. Polym. Sci.* 75, pp.406, 2000.
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Hong Zhao

[Regular member]



- Jul. 1998 : Nanjing Univ., hina, B.S.
- Jan. 2000 ~ Mar. 2008 : China Coal Energy Group Co., Ltd., Engineer
- Mar. 2008 ~ February. 2010 : Soonchunhyang Univ., M.S.

<Research Interests>

Friendly-environmental materials, Functional coating

Jin-Wook Ha

[life member]



- Feb. 1986 : Yonsei Univ. Chemical Engineering, B.S.
- Aug. 1990 : Univ. of Illinois (USA) Chemical Engineering, M.S.
- May 1993 : Univ. of Illinois (USA) Chemical Engineering, Ph.D.
- Mar. 1995 ~ current : Soonchunhyang Univ., Dept. of Energy Environmental Engineering, Professor

<Research Interests>

Friendly-environmental materials, Functional coating, Photocatalyst, Air and water pollutants treatment