

자외선 경화코팅 필름-기질 계면에서의 주름현상에 대한 연구

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Experimental Studies of Wrinkle Formation in the UV Cured Coating Around Film-Substrate Interface

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요 약. 자외선 경화코팅 필름-기질 계면에서의 건담성에 대하여 조사하였다. 특히, UV 경화 우레탄 아크릴레이트계 배합물에서 모노머 및 올리고머의 코팅필름 주름현상에 미치는 영향을 조사하였다. 실험결과, 주름현상은 DMTA이 손실모듈러스 피크가 넓고 shoulder가 있을수록 덜 나타났다. 특히, 변성된 방향족 우레탄 아크릴레이트를 지방족계에 첨가하므로써 hard하면서도 flexible한 코팅필름을 얻을 수 있음을 알 수 있었다. 따라서 주름현상 방지효과는 저온에서의 높은 손실모듈러스값 때문인 것으로 나타났다. SEM 및 instron 실험결과도 위의 결론을 입증하고 있음을 알 수 있었다.

ABSTRACT. The durability of UV radiation cured coatings near the film-substrate interface has been studied. Particularly, the influence of the reactive diluent and oligomer in the UV-cured urethane acrylate formulation on the wrinkle formation of coating films was investigated. Results showed that wrinkle resistance increases when DMTA loss peaks of coating network are broad and has shoulder. When modified aromatic urethane acrylate oligomer is used to replace the aliphatic one, resulting cured network provides coating film of high hardness and flexibility. Therefore, the high values of loss modulus as low temperature are considered to be the main reason for wrinkle resistance improvements. The SEM and instron data support above conclusion.

INTRODUCTION

The environmentally safer coating (ESC) system are getting popular due to the global regulations to reduce the volatile organic components in coating formulations. Among the ESC systems such as Radiation cured, water based, high solid, powder, and supercritical carrier coatings, UV radiation cured coating system continues to have the brightest future¹⁻⁴.

The present popularity⁵⁻⁷ of UV radiation curing originates from following points⁸. First, UV curables are comprised of 100% reactive components which provide for environmentally acceptable coating. Second, UV curing system is energetically

efficient requiring a small fraction of the power normally consumed in thermally cured coatings. Finally, UV curables can be easily formulated to meet a variety of applications since functionalized monomers and oligomers are available covering a wide range of properties.

One of the prime application areas for UV curable coatings is clear coats on substrates ranging from metals and wood to floors and paper. Each of these substrates demands a different set of properties from the UV curable coatings. For example, coating on metallic substrates must have good adhesion and be able to resist deformation induced by stress experienced during use. On the

other hand, coating on wood that is exposed outdoors must extend and retract to keep up with dimensional changes caused by water absorption and desorption by the wood. If permanent deformation of the coating occurs, a wrinkle will form when the wood contract. Possibly, a recoverable elongation is preferable for exterior use on wood. Therefore, coating scientist should consider what kind of elongation they want in their coatings.

Recently, outlest for radiation curable coatings on the plastic substrates are rapidly growing. However, the durability of UV radiation cured coatings near the film-plastic substrate interface is not fully understood yet. In this study, the influence of the reactive diluent and oligomer in the UV-cu-

rable urethane acrylate formulation on the wrinkle formation of coating network was investigated.

EXPERIMENTAL

Commercially available monomers and oligomers shown in Table 1 and 2 were used in this experiment except for aromatic urethane acrylate oligomer prepared for coating D. Hydroxy propyl acrylate (HPA: OSAK YUKI Co.), Caprolactam Modified Propyl Acrylate (CMHPA: UCC's M-100), Tripropylene Glycol Diacrylate (TPGDA: Sartomer Co.), Polyethylene Glycol (400) Diacrylate [PEGDA (400): Sartomer Co.], and Trimethylolpropane Triacrylate (TMPTA: Sartomer) were used for molecular diluents. Sartomer's CN966 and CN 970 were used for aliphatic and aromatic urethane acrylates, respectively. Specially modified aromatic urethane acrylate oligomer was used for coating D⁹. 1-Hydroxyl-cyclohexyl-phenyl-ketone (Ciba's Irg. 184) and Silicone type BYK's 307 were used as a photoinitiator and an additive, respectively. The liquid formulation as shown in Table 1 were applied to the PVC substrates and the wet films were exposed to UV irradiation controlled in 80 W/cm of medium pressure mercury lamp. Dynamic mechanical spectra were recorded using a dynamical analyzer (Dupont DMA Model 983) at temperatures between -80 and +120°C. The measurements were carried out at a heating rate of 5 °C/min by using the resonance mode. The tensile strength and elongation at break of the coating film were determined on a Instron testing machine (Model 1123) at room temperature at a crosshead speed of 20 mm/min using dumbbell-shaped spe-

Table 1. The composition of UV-cured coating formulations

Formulation	Coating A	Coating B	Coating C	Coating D
Aliphatic oligomer	51	48	50	48*
Mono-Monomer 1 (HPA)	32	16	28	16
Mono-Monomer 2 (CMHPA)	0	16	0	16
Di-Monomer 1 (TPGDA)	10	11.5	0	11.5
Di-Monomer 2 (PEGDA)	0	0	17.5	0
Tri-Monomer (TMPTA)	3	3	3	3
Initiator	3.5	5	4	5
Additive	0.5	0.5	0.5	0.5

*Hybrid system composed of aliphatic and aromatic oligomer.

Table 2. Surface and bulk properties of UV-cured coatings

Property	Coating A	Coating B	Coating C	Coating D
Pencil hardness	H	HB	B	HB
Solvent resistance	Excellent	Good	Bad	Excellent
Adhesion on PVC	100/100	100/100	100/100	100/100
T _g	34.8	17.8	8.6	20.8
Elongation (%)	24.4	8.9	8	13.2
Tensile strength (kg/mm ²)	1.52	0.28	0.19	0.61
Young's modulus (kg/mm ²)	25.8	3.3	2.4	8.2
Wrinkle resistance	Bad	Good	Excellent	Excellent

cimens. Finally, crosssection of the coating-substrate multilayers were characterized by scanning electron microscopy (Cambridge 5-360 SEM).

RESULTS AND DISCUSSION

The results of the investigations of the UV cured coating films are summarized in *Table 2*. Let us first consider the effect of the monomer functionality on the coating properties. Comparison of coating A with coating C shows that the use of a lower-functional diluent improves wrinkle resistance. As one uses the mono- and di-functional monomers only, however, resulting films may have a poor resistance properties as shown in case of coating C. On the other hand, coating B shows relatively good surface properties resulting from slight different formulation compared with that of coating A by replacing the portion of the mono-functional monomer (HPA) with CMHPA. However, the elongation and tensile strength of resulting film is still too poor. As can be seen in *Table 2*, it is very easy to develop flexible films that are to have little or no solvent resistance¹⁰. Obviously, coating film that are flexible and also hard to have a solvent resistance are a greater challenge^{11,12}. An example of work directed at balancing properties is the case of coating D in *Table 2*. One can notice that coating D has both good surface properties and good mechanical properties. Unlike the coating A, B and C, coating D has a hybrid oligomer in its formulation.

The results presented above indicate that the modification of oligomer in the coating formulation is more efficient than that of monomer for the wrinkle resistance. Because such a structure-property related phenomenon is of a great fundamen-

tal and practical interest, let us consider this behavior in conjunction with thermal mechanical data. It was found from DMTA results that the most striking difference is for the loss modulus peaks of coating film as shown in *Fig. 1*. One can notice that DMTA loss peaks (E'') from the Coating D is broader than the others. It indicates that coating D has a broader distribution of lengths of chains between network junction points which results in broader loss peaks than the others. Partial phase separation can also cause this broadening. Generally, coatings which give these broad loss peaks have better combination of flexibility and hardness than is achievable with sharp loss peaks¹³. Data in *Table 2* support this idea that both hardness and flexibility of coating D are excellent compared to those of coatings A-C.

In an effort to understand the relationship between structure and properties of the coating network, the effect of different oligomer on the DMTA loss peaks were studied. *Table 3* lists the compositions used in this study along with key

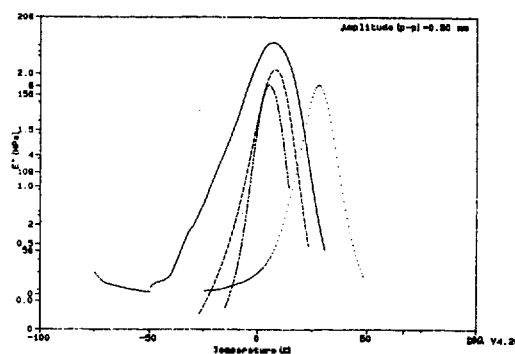


Fig. 1. E'' vs. temperature plots of UV-cured coatings. (····) Coating A, (----) Coating B, (- · - ·) Coating C, (—) Coating D.

Table 3. Composition and properties of UV cured coatings

Sample	Aromatic PUA	Aliphatic PUA	T_g	Tan delta (max)	E' (min)
A1	0	50	27.0	0.42	0.035
A2	10	40	18.3	0.33	0.021
A3	25	25	23.8	0.49	0.020
A4	40	10	14.1	0.34	0.014
A5	50	0	22.3	0.39	0.010

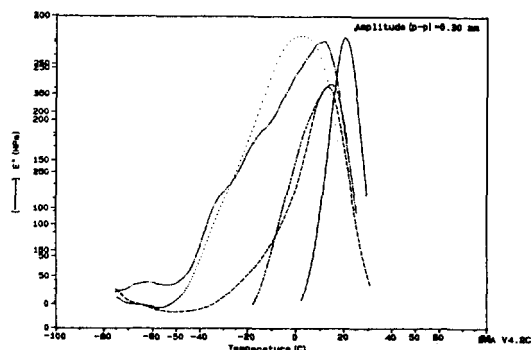


Fig. 2. E'' vs. temperature plots of UV-cured coatings. (—) A1, (---) A2, (-·-·) A3, (····) A4, (- - -) A5.

properties of coating film. The amount of monomer and additives was the same in each formulation. The comparison of Tan Delta (max) and E' (min) shows that loss peaks are again the key parameter. Fig. 2 presents the DMTA loss peaks for Samples A1-A5. With increasing aromatic components of oligomers, loss peaks are getting broader. With pure aromatic oligomer, such as for sample A5, loss peaks produce more than one shoulder peaks which indicates the micro phase separation. If phase separation is complete enough so that distinct domain exist, two transitions are observed instead of a single broadened transition. In addition to the peak for the main transition, certain coating networks have low temperature loss peaks even in the absence of domain structure. Such peaks arise because a part of the molecular structure can undergo molecular cooperation motion at low temperatures. If the part of the structure that causes the low temperature peak is in the coating network and if the peak is a strong one, the coating network is likely to have excellent impact resistance. This also supports our explanation for the shoulder peak in the DMA loss peaks of coating D.

At this point, it is appropriate to correlate the durability of coating network around film-substrate interface with the DMTA loss peaks to understand the origin of the wrinkle formation from the cyclic bending. Durability of coating network around film-substrate interface is affected by adhesive and cohesive sources. Although adhesion

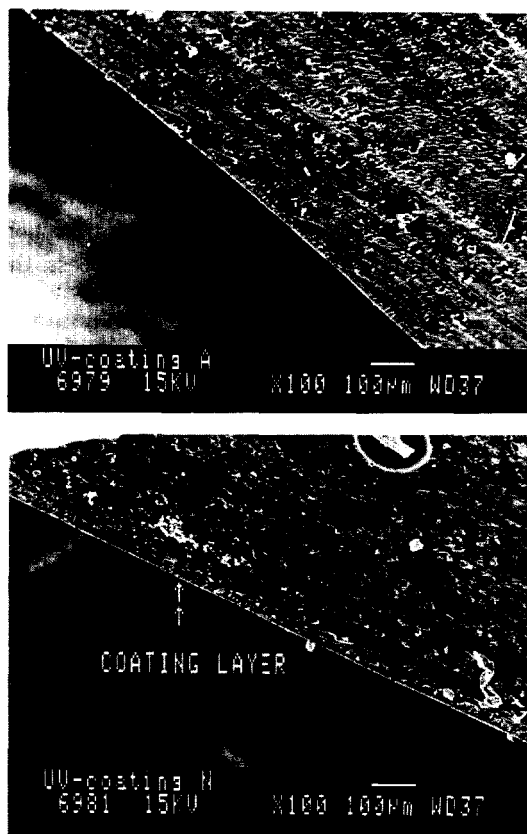


Fig. 3. SEM photographs of coating B (Top) and coating D (Bottom).

data of Table 2 rule out the adhesion source responsible for the wrinkle formation, more direct evidence is necessary to understand the mechanism of wrinkle formation. SEM photographs of coating B and coating D are shown in Fig. 3 (A and B). It is interesting to notice that the coating B appears quite different from the coating D when observed under the SEM. Coating B introduced the wrinkling from the bending as clearly shown in the Fig. 3(A). The coating A appeared to be similar in failure mode with the coating B. In contrast to the coatings A and B, coating D did not introduce the wrinkling from the same bending deformation as shown in Fig. 3(B). Again, coating C appeared to be quite similar in failure mode with coating D.

It is appropriate to ask why hard coating D responds the same way as soft coating C to the defor-

mation. One explanation is that coating D has a greater degree of freedom of movement as much as coating C has. As mentioned in the discussion of DMTA, origins of good wrinkle resistance for coating B and coating D are totally different each other. Coating D has flexibilizer in the coating network which function by broadening the transition or introducing a low temperature loss process. On the other hand, coating B has network structure which mainly reduces the T_g .

Based on these considerations we are in a position to address the factors that affects the wrinkle resistance. The high values of loss modulus at low temperatures are considered to be the main reason for wrinkle resistance improvements. Balancing properties of substrate and film are another factor. Coatings for flexible substrate such as PVC film should have good elongation and tensile strength properties. Hardness and wrinkle resistance are two desirable characteristics of UV curable coatings. However, because hardness is associated with higher T_g and good wrinkle resistance with lower T_g , there is usually a trade-off between hardness and wrinkle resistance. In this study, we have found that the addition of specially modified aromatic urethane acrylate oligomer to the coating formulation otherwise aliphatic urethane oligomer provides coating networks that are substantially harder than comparable coating binders not having aromatic urethane acrylate and have found that this is obtained without substantially raising T_g of the coating binder. The presence of modified aromatic urethane groups also imparts other desirable properties to the formulated coating.

CONCLUSION

Wrinkle formation in the UV curable acrylic

urethane coating to the PVC substrate depends greatly on the cohesive force than adhesive properties. When a specially modified aromatic polyurethane acrylate oligomer is used to replace a portion of aliphatic polyurethane acrylate oligomer in the UV curable coating film, it helps to maintain high surface properties such as hardness and solvent resistance, and increases the wrinkle resistance, subsequently making the coating film useful for a wide range of applications, including PVC flooring.

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