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INFLUENCE OF A POLYURETHANE DIACRYLATE AND HEXANEDIOL DIACRYLATE RATIO ON THE PHOTOCROSSLINKING AND PROPERTIES OF UV-CURED COATINGS

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Abstract. Influence of a polyurethane diacrylate (UDA) and hexanediol diacrylate (HDDA) ratio on the photocrosslinking and properties of the systems based on UDA, HDDA and photoinitiator Irgacure 184 (I.184) has been investigated. It was demonstrated that in the range of the UDA/HDDA ratio from 80/20 to 20/80, the fine, smooth films were obtained when the ratios were from 60/40 to 40/60 and the lower UDA/HDDA ratio the faster conversion of acrylate groups. The acrylate groups in the investigated coatings were converted rapidly, leading to formation of tridimensional polymer networks and change of physico-mechanical properties of the coatings. When the UDA/HDDA ratio changed from 60/40 to 40/60 the relative hardness, impact resistance, flexibility and adhesion of the coatings after 1.2 second of UV-exposure were varied in the range of 0.44 – 0.57; 160-100 kG.cm; 1-2 mm, 2-3 points, respectively, while gloss at 60^o was remained to be 100 %.

Keywords: photocrosslinking, polyurethane diacrylate, hexanediol diacrylate, photoinitiator I.184.

Classification numbers: 2.5.3.

1. INTRODUCTION

Up to now photocuring of coatings based on acrylate compounds has increasingly attracted attention of scientists and producers thanks to distinct advantages of the process such as high productivity, energy save, environmental protection and high performance of the photo-cured products [1-7].

It is well known that a UV-curable coating consists of three main constituents: photoinitiator, UV-reactive multifunctional oligomer and monomer. Among the acrylate oligomers used in UV-curable formulations so far, polyurethane diacrylate is always a good choice for UV-cured products when the combination of the high physico-mechanical properties and superior optical properties and weatherability is needed [1, 5, 6].

Since photocuring reaction and properties of the photo-cured products are much influenced by content and nature of the constituents in the formulation, the question should always thoroughly be investigated to find out the reaction kinetic – structure – properties relationship as well as to design optimal formulation for each concrete application [2-8]. The objective of this work was the study of the influence of the polyurethane diacrylate and hexanediol diacrylate ratio on the photocrosslinking reaction and properties of the UV-cured coatings based on the acrylate compounds and the radical photoinitiator I.184.

2. EXPERIMENTAL

2.1. Materials

The materials used in investigated UV-curable formulations were Ebecryl 284 (Allnex, Belgium), hexanediol diacrylate (UCD Chemical, Belgium) and photoinitiator 1-hydroxy-cyclohexyl-phenyl-ketone with trade name Irgacure 184 (Ciba Specialty Chemicals). Chloroform as a solvent was PA grade from China.

2.2. Samples preparation

UV-curable formulations were made by stirring UDA, I.184 in HDDA to obtain solutions with different contents of the constituents (Table 1).

Table 1. Weight ratio of constituents in investigated systems UDA/HDDA/I.184.

No	UDA/HDDA/I.184	UDA	HDDA	I.184
1	80/20/3	80	20	3
2	60/40/3	60	40	3
3	50/50/3	50	50	3
4	40/60/3	40	60	3
5	20/80/3	20	80	3

The coatings were applied onto substrates by using Spiral Applicators (Erichsen) of 10 µm (for IR analysis) or 30 µm (for performance evaluation of coatings).

2.3. UV-exposure

Investigated coatings were exposed to UV-irradiation by use of a Fusion UV (model F300S, USA) having medium pressure mercury lamps with light intensity of 250 mW/cm^2.

2.4. Analysis

IR analysis was realized by using an FT-IR spectrophotometer (Nexus 670 from Nicolet).

Gel fraction, swelling degree were evaluated by methods reported in published work [8]. Persoz hardness, impact resistance, adhesion on steel substrate, flexibility, gloss of UV-cured coatings were determined by means of suitable testers in accordance with recommended

standards like: Pendulum damping tester (model 300), NFT 30-16; impact tester (model 304), ISO 6272, Elcometer cross Hatch cutter, ISO 2409, flexibility tester (model ШГ – 1), ГОСТ 6806 – 53, gloss meter (Picogloss 3, model 503), ISO 2813. Relative hardness was the quotient of the Persoz hardness of the cured coatings and 425s (Persoz hardness of a glass standard).

3. RESULTS AND DISCUSSION

3.1. IR spectra of investigated coatings

IR spectra of investigated coatings before and after UV-irradiation as well as changes of their absorption bands during the process are presented in Fig. 1 and Table 2.

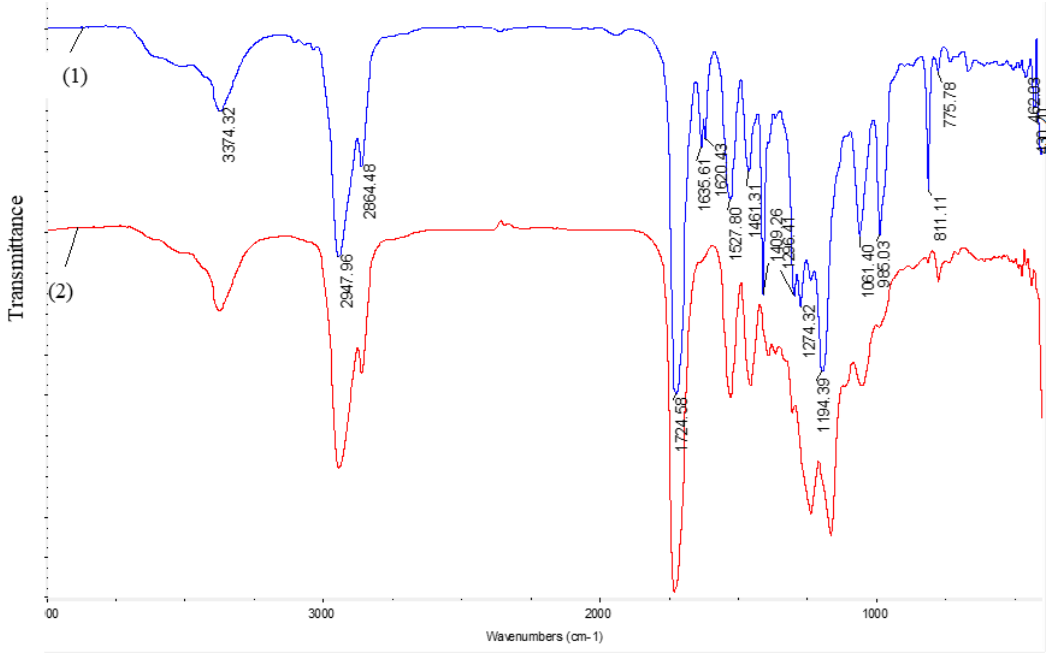

Figure1. IR spectra of the system UDA/HDDA/I.184 = 50/50/3 before (1) and after 4.8s (2) of UV-exposure.

Table 2. Variation of functional and atom groups after UV-exposure.

No	Wavenumber (cm^{-1})	Functional and atom groups	Change
1	3374	N-H stretching (in Urethane groups)	Unchanged
2	1725	C=O stretching	Unchanged
3	1620	Acrylate C=C stretching	Sharp decrease
4	1409	Acrylate scissoring	
5	985	C-H out of plane bending of acrylate groups	
6	811	Acrylate twisting	

It can be seen from Fig. 1 and Table 2, UV-exposure led to sharp decrease of the intensity of the absorption bands at 1620, 1410, 985 and 811 cm^{-1} characteristics for acrylate double bonds [2]. At the same time, absorption bands at 3374 and 1725 cm^{-1} attributed to N-H bonds in urethane groups and carbonyl groups, respectively, remained unchanged. Among them, absorption bands at 1725 cm^{-1} and 811 cm^{-1} are very well separated from the others in the spectra. Hence, they were used for evaluation of the change of acrylate groups during the UV-irradiation by internal standard method [2,8].

3.2. Change of acrylate groups

Variation of acrylate groups in the coatings with various UDA/HDDA ratios are demonstrated in Fig. 2. It can be seen from the figure that most of acrylate groups were converted after 0.15 second of UV-exposure (70 % in coating with UDA/HDDA = 20/80 and 80 % in the other coatings). It should be noticed that molecular weight of UDA in Ebecryl is 1200 [3], much greater than the one of HDDA (226) and the acrylate contents of the coatings having UDA/HDDA ratios of 80/20, 60/40; 50/50; 40/60 and 20/80 were 3.11; 4.54; 5.26; 5.98 and 7.41 mol/kg, respectively. So, in the beginning stage of the reaction, the higher HDDA content in coating formulation, the faster conversion of acrylate double bonds. The above mentioned can be explained by the fact that the addition of HDDA into coating formulations increased their acrylate group content, decreased their viscosity, thus, enhanced mobility of molecules in the systems and favored their reaction.

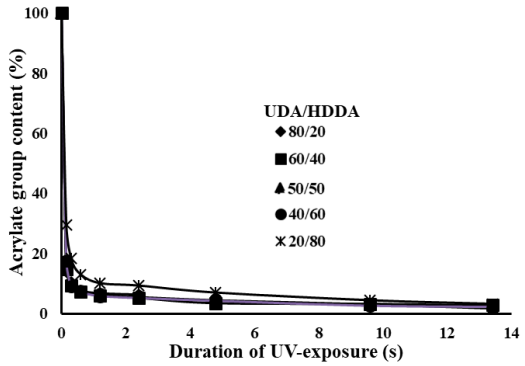

Figure 2. Change of acrylate group content in coatings with various UDA/HDDA ratios.

3.3. Physico-mechanical properties

3.3.1. Relative hardness variation

Difference in molecular weight and polarity between UDA and HDDA led to difference in viscosity and polarity of formulations having various UDA/HDDA ratios and consequently, their unlike film forming possibilities in defined substrates. It was recognized that formulations having the ratio UDA/HDDA of 60/40; 50/50 and 40/60 were easily applied onto glass to form smooth wet coatings when the wet coatings of the formulation with the ratios UDA/HDDA of 80/20 and 20/80 were not so fine due to high viscosity (UDA/HDDA = 80/20) or large difference in polarity compared with glass (UDA/HDDA = 20/80). The variation of relative hardness of the coatings with various UDA/HDDA ratios upon UV-exposure are shown in Fig. 3.

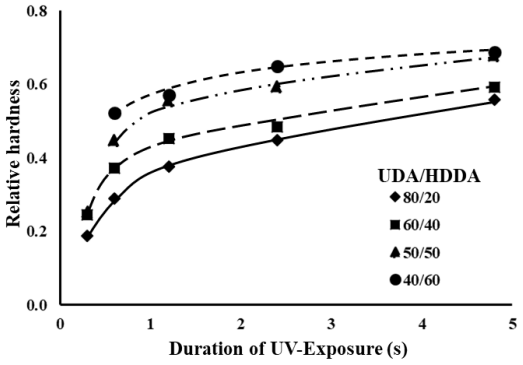

Figure 3. Variation of relative hardness of investigated coatings.

It is clear from the figure, the higher HDDA content in coating formulation the faster increase of the relative hardness and the harder UV-cured coating after definite duration of UV-irradiation. These were in good agreement with the results of investigation of conversion of acrylate groups during UV-exposure. The higher HDDA content in coating formulation, the faster acrylate conversion and as a result the faster crosslinking in the system, which led to its higher relative hardness. Since formulation with ratio UDA/HDDA = 80/20 was too viscous to form a good coating, wet coating having ratio UDA/HDDA = 20/80 was shrank when applied onto glass, the formulations with ratios UDA/HDDA = 60/40;50/50 and 40/60, providing good films, were selected for further investigation.

3.3.2. Some other physico-mechanical properties

Some other physico-mechanical properties of coatings with various UDA/HDDA ratios such as impact resistance, flexibility, adhesion, gloss after 1.2 and 2.4 seconds of UV-exposure are presented in Table 3.

Table 3. Some of physico-mechanical properties of investigated coatings.

UDA/HDDA ratio	*Duration of UV-exposure (s)*	*Impact resistance (kG.cm)*	*Flexibility (mm)*	*Adhesion (point)*	*Gloss*		
					20°	*60°*	*85°*
40/60	1.2	100	2	3	86.8	100	95.9
	2.4	80	3	4	74.2	100	91.9
50/50	1.2	160	1	2	77.8	100	96
	2.4	140	1	2	66.5	96.7	94.6
60/40	1.2	160	1	2	78.4	100	96.7
	2.4	156	1	2	74.9	100	95.6

The data in Table 3 show that the increase of the UDA/HDDA ratio led to increase of impact resistance, flexibility and adhesion but do not influence much on the gloss of UV-cured coatings which was very high for all the coatings. The obtained data can be explained by the fact that increase the UDA/HDDA ratio means increase of UDA content – a constituent with flexible

backbone and polarity suited for coatings on steel with good impact resistance, flexibility and adhesion. It can be noticed also that increase of UV-exposure duration from 1.2 to 2.4 s may decrease some properties because of enhancement of crosslinking density in the coatings.

3.4. Gel fraction and swelling degree

The above mentioned was confirmed by the obtained gel fraction, swelling degree and duration of exposure relationship illustrated in Fig. 4. In accordance with the variation of acrylate groups, mechanical properties during UV-exposure demonstrated in Figs. 2, 3 and Table 3, investigated coating was crosslinked during UV-exposure, resulted in formation and increase of its gel fraction as well as decrease of swelling degree.

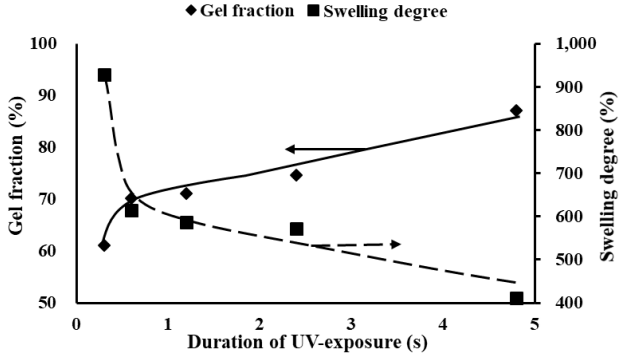

Figure 4. Variation of gel fraction and swelling degree of coating having UDA/HDDA ratio of 50/50 during UV-exposure.

4. CONCLUSION

It was shown that the film forming possibility, photoinitiated crosslinking reaction as well as the properties of the cured coatings on the base of UDA, HDDA and I. 184 were much influenced by the UDA/HDDA ratio. In the investigated range of the ratios, the fine, smooth coatings were formed when the ratios UDA/HDDA changed from 60/40 to 40/60. The reaction of acrylate groups upon UV-exposure led to hardening and formation of tridimensional polymer network in investigated coatings. The lower UDA/HDDA ratio, the higher acrylate group content in the coating formulation and the faster conversion of the groups upon UV exposure, the higher relative hardness, impact resistance, flexibility and the lower adhesion of the cured coatings while the gloss was remained excellent. So that, the properties of the cured coatings can be adjusted to meet the diverse demands of the practice. Formulations having the UDA/HDDA ratios ranged from 40/60 to 60/40 can be used as high performance coatings and adhesives.

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