

Next Generation of UV-Curable Cellulose Esters

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Abstract

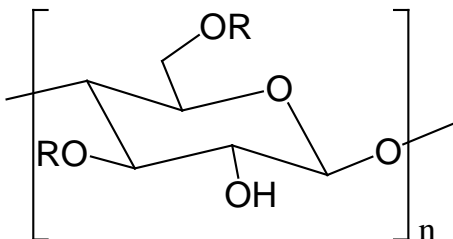
New generation of UV-curable cellulose ester additives and binders provide improved surface hardness and solvent resistance in hard coating and ink applications. UV-curable cellulose ester additives do not disturb clarity and therefore they are excellent additives for clear, very low haze coatings and glossy inks. Their effect on rheology, adhesion, and chemical resistance will be discussed.

Introduction

Cellulose esters have been used in the coatings industry for years to provide improved performance properties.¹ Cellulose esters are made from a renewable structural polysaccharide; cellulose which is one of the most abundant organic chemical in nature. Cellulose esters are used as an additive, reactive resin, or film former. Major benefits are improved cratering, leveling, sprayability, resistance to yellowing, and good viscosity control.²

Commonly used cellulose esters in coating applications are cellulose acetate (CA), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), and nitrocellulose. Properties provided by cellulose esters can be controlled by varying the type and degree of substitution, hydroxyl content and molecular weight. Structure of cellulose esters is as given as in Figure 1 where R can be hydrogen, acetyl, propionyl, or butyryl.

Figure 1. Structure of Cellulose Esters



Introduction of acrylic functional pendant substituent to a cellulose ester provides greater hardness and more scratch and solvent resistance when compared with unmodified cellulose ester in UV-cured coatings. By varying the functionality, type, and amount of substituent, a wide range of properties can be obtained. Commercially available acrylamidomethyl functional cellulose esters (AAECs) are typically used in formulations at 2-10% by weight.³ They are used in coatings and inks as reactive thickeners and adhesion promoters. When compared to coatings formulated with silica additives, coatings formulated with cellulose ester additives have less haze.

As plastics replace glass in many applications, the need for scratch- and chemical-resistant coatings increase. New modified cellulose esters are designed to improve scratch resistance and create impact-resistant coatings.

Experimental

All oligomers were analyzed with gel permeation chromatography (GPC) using a Polymer Labs PL-GPC 50 equipped with RI detector and mixed D-columns. Formulations were mixed using a FlackTek DAC 150.1 FVZ SpeedMixer at 3000 rpm for 2.5 minutes. Viscosities were measured at 25°C using a Brookfield CAP 2000+ viscometer. Formulations were applied on to substrates with a draw down bar to obtain 0.5 mil dry thickness. Formulations were cured after 10 minute of application using a Dymax UVCS conveyer equipped with a Fusion 300 H-bulb. Belt speed was 10 ft/min.

Pencil hardness of the coatings was tested according to ASTM D3363. Direct impact resistance of the coatings was tested on polycarbonate (PC) substrates based on ASTM D2794 with a 2 lb. indenter punch. Maximum of 49" height was tested. Cylindrical mandrel bend testing of coatings on steel panels were performed based on ASTM D522. The minimum separation distance of cracking the coatings was recorded. Crosshatch adhesion was tested in accordance with ASTM Method B2197 on polycarbonate substrates. Chemical resistance to solvent was determined in a manner based on ASTM Method D5402 using methyl ethyl ketone (MEK) as the solvent. A maximum of 200 solvent double-rubs were performed.

Results and Discussion

Description of the UV-Curable Cellulose Esters Synthesized

Urethane acrylate functional cellulose esters (UACEs) were synthesized and compared with an acrylamido functional cellulose ester. All of the UACEs contain the same amount of urethane groups bonded to the cellulose ester backbone. Figure 2 demonstrates the pendant urethane and acrylate groups to the cellulose ester backbone. Cellulose ester and acrylate amounts were adjusted to observe their effect on coating properties. Table 1 shows cellulose ester weight percentage of the UACEs and the ratio of equivalents of acrylate groups to urethane groups. All of the UACEs were prepared or diluted with n-butylacetate to 40% solids concentration.

Figure 2. Representation of UV-Curable Cellulose Esters

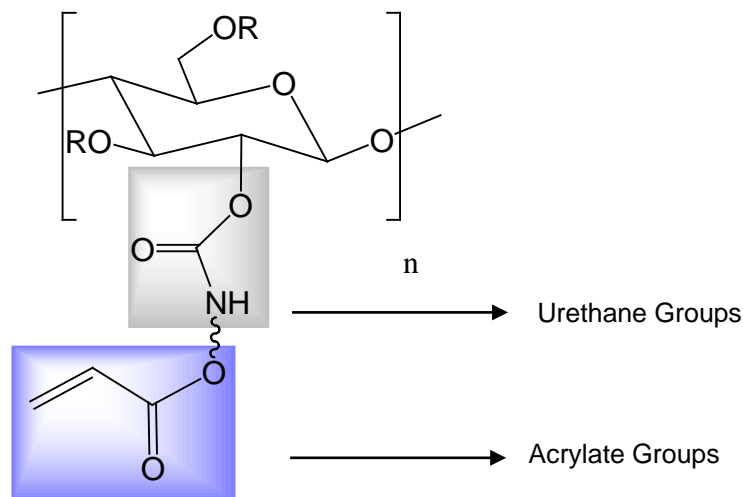


Table 1. Urethane Acrylate Functional Cellulose Esters (UACEs)

	Cellulose Ester Backbone Weight %	Ratio of Acrylate/Urethane	Molecular Weight (Daltons)	Viscosity at 50°C
UACE1	74	0.5	53000	15000
UACE2	94	1	52000	26000
UACE3	47	1.5	54000	1500
UACE4	87	0.5	57000	27000
UACE5	47	0.67	300000	16000

UACEs were formulated to 40% solids with 4% α -hydroxyketone type photoinitiator (PI) and butyl acetate and then dried at 25°C, 20% relative humidity. Tack-free coatings formed were tested before curing and after curing. In Table 2, the difference between uncured and cured properties of UACEs can be seen. The pencil hardness of the uncured coatings were between HB and F hardness. After UV-curing, all of the coatings' pencil hardness was increased. The most increase was with UACEs with relatively low amount of cellulose ester backbone (UACE3 and UACE5). UACE with highest acrylate content (UACE3) showed the highest improvement in impact resistance, probably due to extent of crosslinking. Crosshatch adhesion on PC was remarkably increased with UACE3 and UACE5 after curing.

Table 2. Difference Between Uncured and Cured Properties of UACEs

	Pencil Hardness		Impact Resistance (inch)		Crosshatch Adhesion	
	<i>Uncured</i>	<i>Cured</i>	<i>Uncured</i>	<i>Cured</i>	<i>Uncured</i>	<i>Cured</i>
UACE1	HB	F	20	25	0B	0B
UACE2	F	H	24	37	5B	1B
UACE3	HB	H	15	>49	0B	5B
UACE4	F	H	20	21	3B	0B
UACE5	HB	H	>49	>49	0B	5B

Substrate: PC Thickness of the coatings: 0.5 mil

In a model soft coating formula (Table 3), various UACEs were compared with an acrylamidomethyl functional cellulose ester (AACE) and a control without any UV-curable cellulose ester. Results are given in Table 4. All of the coatings' pencil hardnesses were higher than the control. Most of the UACEs gave higher pencil hardness compared to AACE, probably due to urethane bonds. All of the coatings had good impact resistance and adhesion to polycarbonate.

Table 3. Model Soft Coating Formula

	Model Formula	Control
UACE or AACE	24%	-
Polyurethane triacrylate	40%	52%
1,6-hexanedioldiacrylate (HDDA)	32%	44%
Photoinitiator	4%	4%

Table 4. Properties of UACEs in Model Soft Coating Formula

	Pencil Hardness	Impact Resistance (inch)	Crosshatch Adhesion
UACE1	H	>49	5B
UACE2	F	>49	5B
UACE3	F	>49	5B
UACE4	F	>49	5B
UACE5	HB	>49	5B
AACE	HB	>49	5B
Control	2B	>49	5B

Substrate: PC Thickness of the coatings: 0.6 mil

In a hard coating formula, the dendritic acrylate (DA) levels of a UACE was varied to see the effect on coating properties. Two different amounts of dendritic acrylate were substituted with UACE3 as given in Table 5. Replacing 12% of DA with UACE3 improved the mandrel bend resistance significantly and also improved impact resistance slightly (F-1 vs. F-3). This is probably due to high molecular weight of UACE3 (50,000 DA). One significant result of this test is that pencil hardness did not change with addition of 12% UACE3. This might be due to hardness provided by the cellulose backbone. However, further replacement of DA with UACE3 negatively affected pencil hardness, impact resistance, and mandrel bend resistance (F-2 vs. F-1 and F-3). Therefore, hard coating formulations should be optimized to find the best concentration of UACEs.

Table 5. Hard coating formulations with UACE3

	F-1	F-2	F-3
UACE3	12%	24%	-
Dendritic Acrylate (DA)*	84%	72%	96%
PI	4%	4%	4%

Table 6. UACEs in hard coating formulations

	Pencil Hardness	Impact Resistance	Crosshatch Adhesion	Mandrel Bend Resistance	MEK2RUBS
F-1	2H	19	5B	passed at 0.25"	>200
F-2	H	13	5B	failed at 0.75"	>200
F-3	2H	16	5B	failed at 0.5"	>200

Conclusions

Urethane acrylate modified cellulose esters provide improved surface hardness compared to acrylamidomethyl functional cellulose ester. They are capable of improving the pencil hardness of soft coatings without reducing impact resistance. In hard coating formulations they can be used to improve flexibility and impact resistance without changing pencil hardness. UV-curable cellulose esters do not disturb clarity and therefore they can be used as additives for inks and optically clear coatings.

References

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- ³ Dymax Corporation. (2013). Jaylink® UV-Curable Additives Enhance Surface Hardness [press release]. Retrieved from http://www.dymax-oc.com/pdf/press_release/p299_jaylink_additives.pdf



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