“Novel acrylate resin for better UV protection”

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Abstract:
A novel acrylate was synthesized and used as an oligomer in UV curable formulations. Oligomer was suitably formulated with different monomers and photoinitiators. These formulations were tested for curing speed, glass transition temperature (Tg), % gloss retention, yellowing index, flexibility, adhesion and weatherability after exposing 1000 hours to UV.

Introduction:
UV curing has found an increasing number of industrial applications over the years and will find more applications area in the years to come. The major reasons for this are its unique benefits like solvent free formulation (Zero VOC), high production output, low temperature processing, low energy consumption etc. In addition to these benefits, additional properties desired out of UV cured coatings are chemical resistance and UV protection. Coating companies all over the world are currently developing coating system for outdoor application with good weatherability. Coatings exposed to outdoor use are subjected to especially harsh weathering conditions like UV light, oxygen, moisture and other pollutants. The possible approach to stabilize coatings for such conditions can be usages of stabilizer whose filter effect protects the substrate against color change and photochemical degradation. However, much research work is in progress to improve the resin/ monomer backbone to protect coating against UV. This study is focused on development of novel acrylate resin which is based on cycloaliphatic backbone. This resin was suitably formulated and it’s physical, chemical, mechanical properties and weatherability of cured films was tested using different monomers and photoinitiators.

Experimental:

Materials:
The materials used for present study with commercial source and abbreviation are listed in Table 1 for ready reference. Acrylate oligomer resins and monomers used in present study were prepared in laboratory and their physical and chemical characteristics are described in Table 2.

Blending procedure:
To facilitate material handling, oligomers were warmed prior to blending. To avoid gelation, temperature was maintained less than 50^{o} C. The other ingredients were added and mixed properly, followed by cooling to less than 40^{o} C for better storage stability.

Test specimens:
Films of 1 mil thickness was prepared on Aluminum foil using drawdown applicator and cured further by exposing to UV in Fusion UV system.

Curing Unit:
A laboratory model from Fusion UV System Inc. was used for curing the test specimens. Unless otherwise stated, all the curing was done by using specified conveyor speed under one medium vapor pressure Hg lamp of 80 dy/ $in^{2.}$

QUV test chamber:
QUV solar eye was used for accelerated weathering test.
Bulb: QFS lamps (UV-B-313)
Test conditions: A cyclic program of 4 hours UV radiation at 50^{o}C followed by 4 hours condensation (no UV) at 50^{o}C.
Irradiation: 0.55

Measurements:

Physical property:
All physical properties were tested as per ASTM/DIN/Company internal standard method.

Gloss measurement:
60^{o} gloss was measured with a micro-Tri-Gloss meter from BYK-Gardener. % Gloss retention was calculated by dividing the gloss reading at a certain time by the gloss reading at time zero.

Yellowing measurement:
The yellowing property of a film was expressed by the total color difference (ΔE) , which was measured by color guide sphere from BYK-Gardener[d /8 ^{o} spin] and was calculated by following equation: $\Delta E = \sqrt{[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]}$

Mechanical Properties test:
Flexibility was measured by using 3.7mm cylindrical mandrel.

Solvent resistance test:
Methyl ethyl ketone (MEK) solvent resistance testing was performed and recorded as double rub. Failure was recorded when the film first indicated solvent attack.

Results and discussion:
Two oligomers with different chemical backbone were synthesized and used in different concentrations with acrylate monomer to study its physical, mechanical and wheatherable properties.

Viscosity:
Table 2 shows different physical properties of oligomers and monomers used in present study. The new TAC 1841, cycloaliphatic diacrylate, has significantly lower viscosity compared to TAC 1281, DGEBA diacrylate (Figure 1). Likewise 5 to 10 fold difference in viscosity was observed (figure 2 and 3) when these two oligomers were combined with different monomers in different concentrations. This could be utilized in formulating low monomer content products based on TAC 1841. This shall be advantageous in terms of cost, better mechanical and chemical property.

Curing behavior:
Table 3 represents four different formulation compositions used for present study. The curing behavior of these four formulations is shown in Table 4. MEK double rub analysis measures total crosslink density at a given line speed. It shows that formulation containing N-10A is slower in reactivity compared to 2-EHA. This is possibly due to having a large molecular structure, increases the steric hindrance to obtained required crosslink density. This higher crosslink density in 2-EHA containing formulations results in higher MEK double rub property and higher Tg of cured film compared to N-10A containing formulation.

Physical properties:
Product intended for outdoor application must not only resist yellowing and have a high degree of % gloss retention as this property is a good indicator of moisture resistance. They must possess an ability to maintain their physical properties for the duration of use. It must not become brittle or film should not degrade in terms of micro cracking or chalking. Carefully prepared coating specimens were tested for film flexibility, % gloss retention and yellowing index.

% Gloss retention:
It is the ability of coating to resist color change and is a part of necessary performance parameters. It is also essential that the coating don't chalk or exhibit significant loss on gloss during use. Figure 4 shows the % gloss retention of film at different interval of UV exposure. It indicates that the all systems are having excellent gloss retention property and also indicates that it has excellent moisture resistance. The retention of gloss is mainly due to the chemical structure of TAC 1841 based formulation which are purely aliphatic in nature and avoids formation of aromatic/quinoid moiety responsible for yellowing and chalking of the cured films under UV exposure.

Glass transition temperature (Tg) and flexibility:
Not only is it critical that the coating maintain high level of gloss without significant change in color but, also do not degrade upon long term outdoor exposure. Tg value of the cured material is an indication of mechanical property. Table 4 shows Tg and MEK

double rub values of TAC 1841 containing cured films before UV exposure. Tg and MEK double rub values are increased marginally after 1000 hours UV exposure (Table 5). The increase in these values can be explained by the fact that the residual double bond is undergoing crosslinking process during UV exposure. Table 5 also indicates that the flexibility of the cured film is still maintained at the same level as before UV exposure. It means, the mechanical property and polymer matrix is very much stable under UV exposure and this has an advantage for outdoor applications.

Yellowing Index (YI):

Photoinitiator effect on Yellowing Index:

Photoinitiator is an important factor for developing a formulation with good weathering property. Figure 5 gives comparison of yellowing Index with two very common photoinitator with same TAC 1841 oligomer. Initial yellowing index for Irgacure 184 cured system was very low. However after UV exposure, YI is increases. The explanation is not known. In contrast formulation cured with TPO shows steady yellowing index during UV exposure. The figure also reveals that TPO cured system is maintaining very good non yellowing property for 1000 hours of UV exposure. The study is still continuing for more hours of UV exposure.

Conclusion:

Based on laboratory testing, the data supports the suitability of TAC 1841 oligomer for outdoor applications. It's mechanical property and loss in film gloss data for before and after UV exposure indicates that the film does not degrade over extended period of time. However careful selection of photoinitiator plays an important role for perfect formulations. Data also indicates that TAC 1841 can be use for the low viscosity formulations without using more monomers which can also help to achieve better cost, mechanical properties and chemical resistance.

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Table 1: List of materials used for present study.

Raw material	Chemistry	F	Supplier	Abbreviation
Oligomers				
Oligomer-1	Cycloaliphatic Epoxy Acrylate	2	ABC(T)ED*	TAC 1841
Oligomer-2	Aromatic Epoxy Acrylate	2	ABC(T)ED	TAC 1281
Monomers				
2- ethyl hexyl acrylate	Aliphatic Acrylate	1	ABC(T)ED	2-EHA
Glydex-N-10 acrylate	Aliphatic Epoxy acrylate	1	ABC(T)ED	N-10A
1,6- hexanediol diacrylate	Aliphatic Diacrylate	2	ABC(T)ED	HDDA
Tripropyleneglycol diacrylate	Aliphatic Diacrylate	2	ABC(T)ED	TPGDA
Trimethylol propane Triacrylate	Aliphatic Triacrylate	3	ABC(T)ED	TMPTA
Photoinitiator				
TPO	Aromatic Photoinitiator		Double Bond- Taiwan	TPO
Irgacure 184	Cyclo aromatic Photoinitiator		Ciba	Irgacure 184
Additives				
BYK 333	-	-	BYK- Germany	BYK 333
BYK 088	-	-	Byk Germany	BYK 088

*ABC (T) ED = Aditya Birla Chemicals (Thailand) Ltd. - Epoxy Division

Table 2: Physical property of various raw materials.

Material	EEW, g/eq	Acid value, mg KOH/gm	Color, Gardner	Viscosity @ 25°C, cPs	Inhibitor content, ppm
TAC 1841	55,000	3.0	0.3	39,000	1,000
TAC 1281	10,200	1.0	0.2	3,11,000	1,000
N-10A	22,300	0.5	0.2	128	1,000
2-EHA	-	0.05	0.1	1.7 @ 20°C	500
HDDA	-	0.02	0.1	10	500
TMPTA	-	0.1	0.2	100	175
TPGDA	-	0.5	0.3	15	115

Table 3: Formulations used for present study.

Material	Formulation			
	A	**B**	**C**	**D**
TAC 1841	69.4	69.4	69.4	69.4
N-10A	29.4	-	29.4	-
2-EHA	-	29.4	-	29.4
TPP	0.5	0.5	0.5	0.5
TPO	3.0	3.0	-	-
Irgacure 184	-	-	3.0	3.0
BYK 333	1.0	1.0	1.0	1.0
BYK 088	1.5	1.5	1.0	1.0

Table 4: Curing behavior and property of TAC 1841 oligomer before UV exposure.

Property	Formula			
	A	**B**	**C**	**D**
Line speed (fpm)	70	100	130	143
Gloss (60^o)	100	100	100	100
Yellowing Index	1.11	1.11	-0.57	-0.58
Flexibility (cylindrical Mandrel), mm	3.7	3.7	3.7	3.7
Glass Transition Temperature, Tg^{o}C	28.06	32.32	31.84	40.2
MEK Double Rub	85	97	90	99
Cross-cut adhesion	GT “0”	GT “0”	GT “0”	GT “0”

Table 5: Effect of 1000 hours UV exposures on property of TAC 1841 containing cured films

Property	A	B	C	D
Tg, ^{o}C	33.29	33.76	32.34	41.32
Flexibility, cylindrical mandrel, 3.7 mm	3.70	3.70	3.70	3.70
MEK Double rub	90	100	94	104
Cross-cut adhesion	GT “0”	GT “0”	GT “0”	GT “0”

Figure 1: Effect of temperature on viscosity of TAC resins.

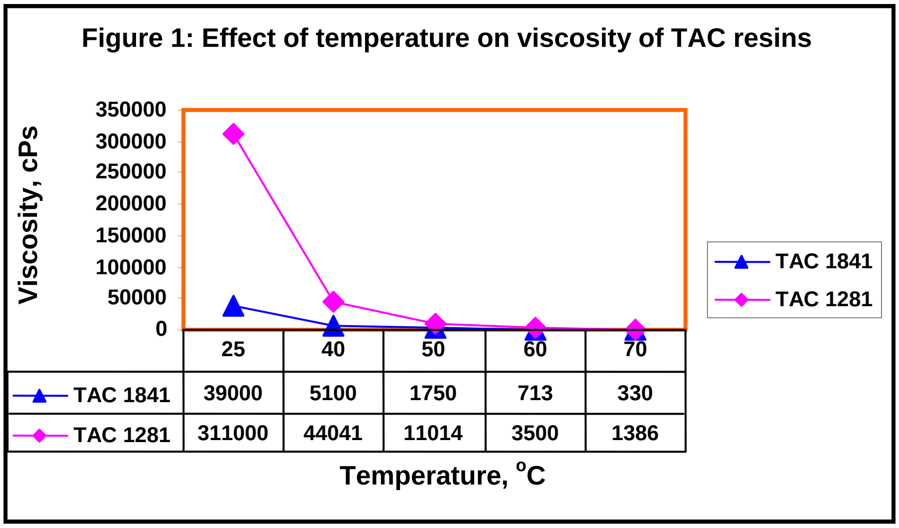

Figure 2: Effect of acrylate monomer concentration on viscosity of TAC 1841 at 25°C.

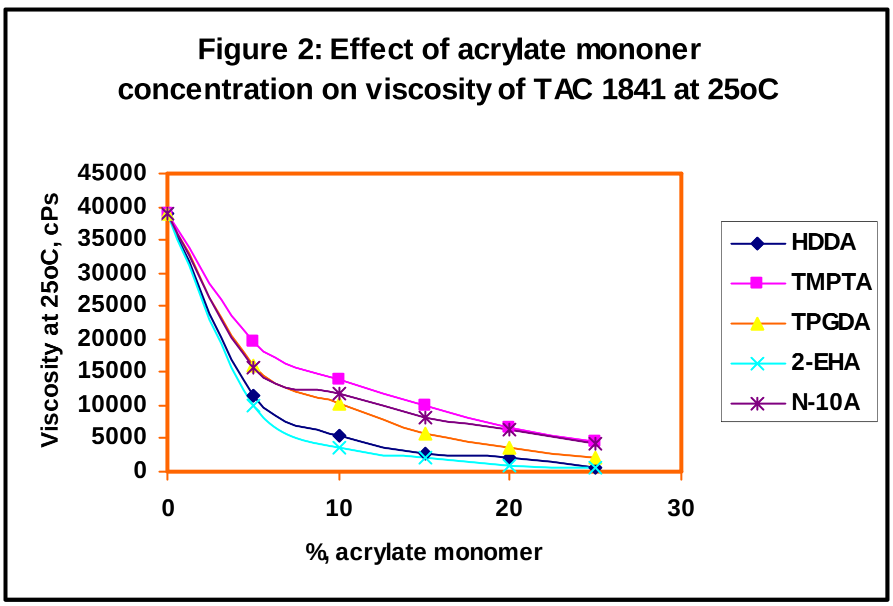

Figure 3: Effect of acrylate monomer concentration on viscosity of TAC 1281 at 25°C.

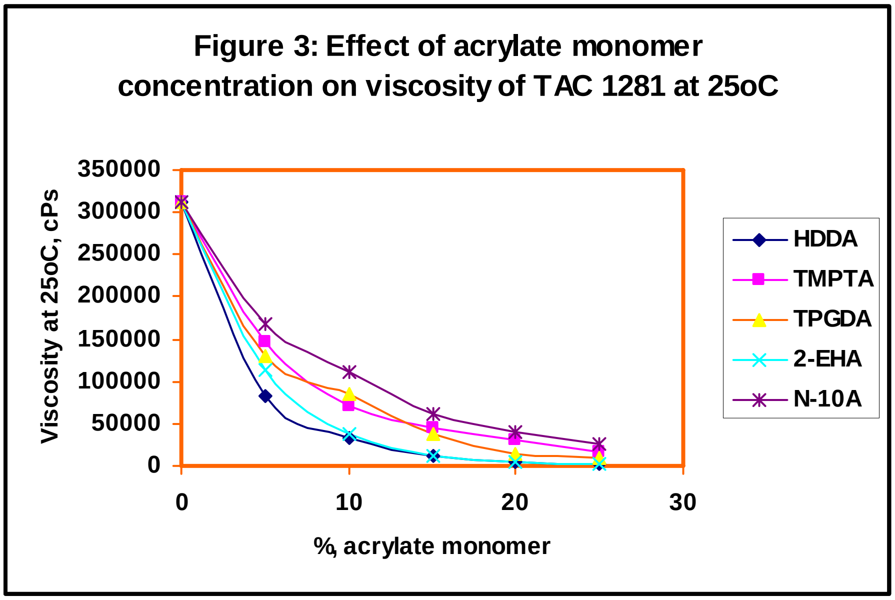

Figure 4: % Gloss retention vs. UV exposure time

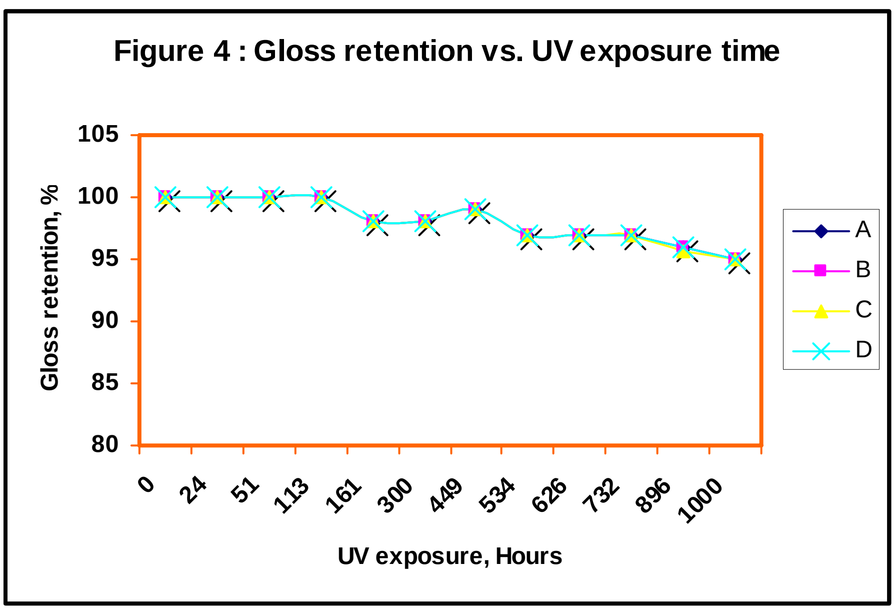

Figure 5: Yellowing index vs. UV exposure time.