Suitability of Energy Curable Oligomers and Monomers as Encapsulants in Photovoltaic Modules

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Introduction

Most thin film photovoltaic (PV) modules contain an encapsulant layer that acts primarily as an adhesive to bond layers together. A good encapsulant will also behave as an electrical insulator, protect components of the PV module by being a "shock absorber" and have the ability to withstand environmental stresses brought on by variations in temperature and humidity. The encapsulant is generally a thermoplastic or thermosetting film that is laminated into the PV structure using heat and pressure; however, an alternate, less energy intensive means of encapsulation is available. In this paper, we will show that UV curable materials are capable of meeting the performance requirements for PV encapsulants. Selected oligomer/monomer blends will be used as interlayers in glass to glass laminates that will then be subjected to thermal cycling, high temperature/humidity exposure, and weatherability along the lines of the testing protocol outlined in IEC 61646, "Thin-film terrestrial photovoltaic (PV) modules – Design qualification and type approval"[i], and be rated on their ability to withstand these severe conditions. Evaluation of the electrical properties of the interlayers will be the subject of a later paper.

Oligomer/monomer selection

A variety of oligomers, covering the main chemistries of UV curable resins, were selected to be part of this study. Seven urethane acrylates (UAs), one polyester acrylate (PEA) and two epoxy acrylates (EAs) were chosen. The urethane acrylates were either aliphatic (based on an aliphatic isocyanate - ALUA) or aromatic (based on an aromatic isocyanate - ARUA). The epoxy acrylates were modified to increase their flexibility as the base bisphenol A diglycidyl ether diacrylate would have been too brittle to withstand the test matrix. The acrylate functionality of the resins varied from 2-6. Within the urethane acrylates, the soft segments were made from either polyether polyols, polyester polyols or caprolactone based polyols. A summary of the neat resin properties appears in Table 1.

The diluents were also selected to span a range of properties. They include an acidic acrylate, a urethane functional acrylate, and multifunctional diluents with acrylate functionality ranging from 1-3. A summary of the diluents and their properties appears in Table 2.

Experimental

Formulations

The selected oligomer and diluent were both charged to a glass container, heated to 60°C and mixed with gentle stirring. When the solution appeared to be homogenous, the photoinitiator (1 phr) and silane coupling agent (1 phr) were added and the formulation stirred an additional 15 minutes.

Glass laminate preparation

Each oligomer/diluent formulation was used to make several 4" x 4" glass laminates. Each lite of glass was thoroughly cleaned and dried, and 30 mil (0.030") spacers were applied to each corner of one of the lites. An amount of the UV formulation sufficient to cover the lite was placed on the glass and the second lite carefully placed on top of the formulation. To ensure a constant interlayer thickness, even pressure was then applied to the second lite so that it was seated on the spacers. The laminates were then cured using two 600 watt/inch electrode-less H type lamps set to 100% output, to give a total UV energy exposure of ~1000 mJ/cm^2. The edges of the laminates were not sealed, so this configuration represents a worst case scenario for the interlayers.

Test protocol

The main three tests that the laminates were subjected to were from sections 10.11, 10.12, and 10.13 of IEC 61646. The Thermal Cycling Test (10.11) subjects the samples to 200 temperature cycles from -40°C to +85°C. The Humidity Freeze Test (10.12) subjects the samples to 10 temperature cycles -40°C to +85°C and 85% RH during the +85°C phase of the test. In the Damp Heat Test (10.13), the samples must withstand 1000 hours @ 85°C and 85%RH. The samples were also evaluated against a Dry Heat Test that requires that the samples withstand 1000 hours @ 85°C and subjected to 2000 hours accelerated weathering exposure.

Equipment

The environmental testing (10.11 – 10.13) was performed in a Weiss Climate Test Cabinet model WK11-600.

Transmission and haze readings were run on a Haze-Gard *plus* haze meter from Byk additives and instruments.

Viscosities were obtained using a Brookfield DV II+ viscometer at 25°C using a #21 spindle.

Samples were subjected to accelerated weathering using a Q-Lab QUV-A Accelerated Weathering tester operating on a cycle of 8 hours QUV @ 60C with no condensation followed by 4 hours no UV @ 50 C with condensation.

Tensile properties were determined in accordance with ASTM D882 using an Instron model 4467 Tensometer.

Color measurements were performed using a BYK Gardner Color guide sphere using a white powder coated panel as background.

Results

As seen in Table 1, the oligomer viscosities can be quite high and cover a broad range, so they were reduced with Diluent 5 to make them easier to handle. A target viscosity of 3000 ± 250 cps was selected for the oligomer blends. In addition to the viscosity, tensile properties of each oligomer blend were also measured. Table 3 contains both the blend viscosities and tensile properties of the oligomer blends. As expected, the UAs show a broad range of tensile strengths and flexibility (% elongation form 1 to 33%).

The modified EAs also have a flexible material (EA1) and a stiffer material (EA2). Not surprisingly, the oligomer functionality has a great effect on the tensile properties, especially the elongation. The higher functionality materials have very low % elongations while the difunctional materials have the higher % elongations.

The diluents were evaluated by making blends using the same oligomer for all samples. The oligomer used was ALUA 6 and the diluent was added to make a 60/40 ALUA 6/diluent blend. The diluents have varying degrees of solvating power, so the viscosity range is broad. The effect of functionality on tensile properties is even more pronounced than with the oligomer samples. The monofunctional diluents have elongations greater than 90% while the higher functional diluents give correspondingly low elongation films, with the trifunctional diluent providing the stiffest film.

The tensile properties of both the oligomer and diluent films will be used to explain some of the results of the remaining testing.

Environmental Testing - Dry Heat, Damp Heat, Temperature Cycling and Humidity Freeze Tests

IEC 61646 instructs the user to assess samples for visual defects, and to test the insulative properties of the complete module at the end of each environmental test. Since we are only evaluating potential encapsulant resins and not full PV modules, no insulation testing was performed. Instead, the laminates were evaluated for changes in color (ΔE), and % light transmission (%T), and examined visually for signs of delamination.

The color and light transmission data for the oligomer blends resides in Table 5. No one oligomer outperformed the others over all four tests. There are instances where an oligomer performs well in one test and is among the poorer performers in a different test. In order to get a sense of which oligomer might have the better overall performance, the oligomers were ranked best to worse for each test and assigned a number from 1 – 9 based on their performance (1 being best). The top performers on each test can then be identified and by combining (averaging) the rankings over all four tests, an estimate of the best overall performers can be made. In terms of color development or ΔE, ALUAs 2, 5, and 4 had the lowest color development in the Dry Heat test; EA 1, and ALUAs 2 and 3 were best in the Damp Heat test; EA 1 and ALUAs 4 and 5 outperformed the other oligomers in Thermal Cycling and EA1, PEA1 and ALUA were identified as most resistant to color change in the Humidity Freeze test. In terms of light transmission or %T, EAs 1, 2 and ALUA 5 faired the best in the Dry Heat test; EA 2, ALUA 6 and EA 1 survived the Damp Heat test best; ALUAs 5, 4 and EA 2 their %T better than the other oligomers in Thermal Cycling while ALUA 5, EA 1 and ALUA 4 showed the smallest change in %T after the Humidity Freeze Test. In summary, EA 1 (modified epoxy acrylate), ALUA 4 (aliphatic urethane acrylate) and ALUA 5 (aliphatic urethane acrylate) were among the top 4 candidates for both minimal color change and minimal change in %T for the environmental tests.

The color and light transmission data for the diluent blends appears in Table 6. Ranking the diluents in terms of their performance for lowest color generation shows that Diluent 4 has the overall best performance, closely followed by Diluent 2. These two diluents are also best in terms of retention of light transmission, although their order is reversed. Overall, Diluent 2 (urethane monoacrylate) and Diluent 4 (cyclic diacrylate) perform the best in the environmental tests.

The laminates made using the oligomer blends were visually assessed for signs of delamination. These results appear in Table 7, along with the tensile data for the interlayers. Whether a laminate underwent delamination during the environmental tests correlates nicely with their tensile properties. The three blends with the highest % elongation (ALUA 5, ALUA 4 and ARUA 1) showed no signs of delamination in any of the environmental tests, the interlayers with the next highest elongations passed 3 of 4 environmental tests and the oligomer blends with the lowest elongations failed in every test.

The performance of the laminates made for the diluent past of this work is shown in Table 8. Here too we see the effects of flexibility on adhesion. The diluent blends with the highest elongation (Diluent 2 and Diluent 1) pass all of the environmental tests. Interestingly, Diluent 4, which is quite stiff, also showed no signs of delamination during the environmental tests. A possible explanation might be that the cyclic diacrylate is known to have low shrinkage, especially when compared to other difunctional diluents. Less shrinkage usually results in lower internal stress in the interlayer, which usually translates to better adhesion.

The dependence of interlayer adhesion on % elongation suggests that some of the other oligomers could be made to pass the testing without delaminating if a more flexible, less functional diluent was used in place of the difunctional acrylate used in this study.

Accelerated Weathering – 2000 hours QUV-A

The environmental tests reveal the resistance of the interlayers to change when exposed to heat or humidity. In addition to these factors, many PV module configurations would require that the interlayers resist degradation when exposed to UV radiation. The Δ E, Δ %T and appearance of the laminates after 2000 hours of QUV-A exposure appear in Table 9 for the oligomer blends and Table 1`0 for the diluent blends. As expected, aliphatic urethanes have the best weatherability of any of the samples. ALUAs 2, 3, 4, and 5 all had extremely low color development, excellent %T retention with no visual defects. In contrast, ARUA, the two EAs and the PEA all had significant color development after exposure to UV energy. Three of the diluents also had excellent performance after being exposed to UV energy. Diluents 2, 3, and 4 had Δ E values < 1, Δ %T < 1 and no visual defects.

Conclusions

- Ten UV curable oligomers were reduced with a UV curable diluent and converted into interlayers in glass to glass laminates and evaluated against environmental and accelerated weathering testing.
- Five UV curable diluents were blended with a UV curable oligomer and converted into interlayers in glass to glass laminates and evaluated against environmental and accelerated weathering testing.
- Three oligomers had good performance in the environmental tests with respect to low color development and retention of high light transmission: EA1, ALUA 4 and ALUA 5 (in order of performance).
- Two diluents demonstrated good performance in the environmental tests with respect to low color development and retention of high light transmission: Diluent 2 and 4.
- Three oligomers showed good resistance to delamination during the environmental tests: ALUA 5, ALUA 4 and ALUA 1.
- Two diluents showed good resistance to delamination during the environmental tests: Diluents 1 and 2.

- Resistance to delamination follows the flexibility (as measured by % elongation) of the interlayers as the best oligomer blends had the highest elongation and the best diluents were the monofunctional diluents, which would be expected to have the highest elongation.
- A difunctional diluent was used to make the oligomer blends. Difunctional diluents will increase crosslinking and decrease % elongation. If a monofunctional diluent had been used for the oligomer blends, it may have been the case that more oligomer blends would have shown better adhesion (less delamination) in the environmental tests.
- As a group, the ALUAs performed best in terms of low color development and % transmission, as expected.
- Within the ALUAs, there was no discernable performance trends based on the soft segment of the urethane. The physical properties of the interlayer were more important than the chemical composition of the oligomer in determining the performance of the oligomer blend.

Resin ID	Description	Soft segment	Acrylate Functionality	Viscosity (cPs, 60°C)
ALUA 1	Aliphatic urethane acrylate	None	6	350
ALUA 2	Aliphatic urethane acrylate	Poly (ether)	6	6000
ALUA 3	Aliphatic urethane acrylate	Poly (caprolactone)	4	135,000
ALUA 4	Aliphatic urethane acrylate	Poly (ester)	2	71,500
ALUA 5	Aliphatic urethane acrylate	Poly (caprolactone)	2	500
ALUA 6	Aliphatic urethane acrylate	Poly (ester)	2	15,000
ARUA 1	Aromatic urethane acrylate	Poly (ether)	2	4500
EA 1	Modified epoxy acrylate	---	2	3500
EA 2	Modified epoxy acrylate	---	2	15,500 (25°C)
PEA 1	Polyester acrylate	---	3	35,000 (25°C)

Table 1. Summary of Oligomer Properties

Table 2. Summary of Diluent Properties

Diluent ID	Description	Acrylate Functionality	Viscosity (cPs, 25°C)
Diluent 1	Acidic acrylate	1	75
Diluent 2	Urethane acrylate	1	40
Diluent 3	Triol acrylate	3	110
Diluent 4	Cycloaliphatic acrylate	2	175
Diluent 5	Diol acrylate	2	10

Table 3. Summary of Oligomer Blend Tensile Properties (Oligomer plus Diluent 5)

Resin ID	Description	Functionality	Oligomer blend visc. (25°C)	Tensile @ break (psi)	Modulus (psi)	Elongation @ break (%)
ALUA 1	Aliphatic UA	6	3250	3,014	468,008	1
ALUA 2	Aliphatic UA (polyether)	6	2820	5,504	175,668	9
ALUA 3	Aliphatic UA (poly caprolactone)	4	2840	4,580	167,882	7
ALUA 4	Aliphatic UA (polyester)	2	3200	1,747	12,838	28
ALUA 5	Aliphatic UA (poly caprolactone)	2	3170	4,235	67,196	33
ALUA 6	Aliphatic UA (polyester)	2	3070	4,950	185,517	12
ARUA 1	Aromatic UA (polyether)	2	3200	1,706	20,763	20
EA 1	Modified EA	2	2750	1,720	13,744	20
EA 2	Modified EA	2	2820	4,368	231,791	7
PEA 1	PEA	3	3200	1,718	21,020	16

Table 4. Summary of Diluent Blend Tensile Properties (Diluent plus Oligomer 6)

Diluent ID	Description	Functionality	Diluent blend visc. (25°C)	Tensile @ break (psi)	Modulus (psi)	Elongation @ break (%)
Diluent 1	Acidic acrylate	1	7200	4,075	114,020	92
Diluent 2	Urethane acrylate	1	5300	1,504	5,709	103
Diluent 3	Trifunctional acrylate	3	14350	5,342	355,535	2
Diluent 4	Cyclic diacrylate	2	20300	6,711	244,713	4

Diluent 5	Difunctional acrylate	2	2800	4,950	185,517	12

Table 5. Environmental Testing of Oligomer Blends - Optical Results

		Dry Heat Test (1000 hours @ 85°C)		Damp Heat Test (1000 hours @ 85°C/85% RH)		Thermal Cycling (200 cycles -40°C to +85°C)		Humidity Freeze (10 cycles -40°C to +85°C/85% RH)	
Resin ID	**Description**	**Δ E**	**Δ %T**	**Δ E**	**Δ %T**	**Δ E**	**Δ %T**	**Δ E**	**Δ %T**
ALUA 1	6f Aliphatic UA	*	*	*	*	*	*	*	*
ALUA 2	6f Aliphatic UA (polyether)	0.26	-5.10	3.62	-7.00	1.94	-11.4	1.56	-10.3
ALUA 3	4f Aliphatic UA (polycaprolactone)	0.74	-7.70	3.78	-1.30	3.05	-6.7	1.10	-3.5
ALUA 4	2f Aliphatic UA (polyester)	0.55	0.80	4.13	-5.10	0.20	-0.1	0.23	-0.3
ALUA 5	2f Aliphatic UA (polycaprolactone)	0.45	0.30	4.26	-1.50	0.63	0.0	0.34	0.2
ALUA 6	2f Aliphatic UA (polyester)	1.41	-5.10	5.43	0.30	1.76	-6.7	1.53	-5.8
ARUA 1	2f Aromatic UA (polyether)	2.03	0.40	3.94	-7.20	3.12	-12.4	1.48	0.7
EA 1	2f Modified EA	1.04	0.00	1.70	0.80	0.17	-0.7	0.15	-0.2
EA 2	2f Modified EA	2.82	0.10	4.12	0.10	1.23	-0.4	3.66	-8.3
PEA 1	3f PEA	0.66	0.50	5.03	-5.90	1.97	1.0	0.21	0.4

* interlayer exhibited multiple cracks when cured and was excluded from the remainder of the study

Table 6. Environmental Testing of Diluent Blends - Optical Results

		Dry Heat Test (1000 hours @ 85°C)		Damp Heat Test (1000 hours @ 85°C/85% RH)		Thermal Cycling (200 cycles -40°C to +85°C)		Humidity Freeze (10 cycles -40°C to +85°C/85% RH)	
Diluent ID	**Description**	**Δ E**	**Δ %T**	**Δ E**	**Δ %T**	**Δ E**	**Δ %T**	**Δ E**	**Δ %T**
Diluent 1	1f Acidic acrylate	1.98	0.10	4.78	-6.60	2.94	-0.5	2.72	-6.0
Diluent 2	1f Urethane acrylate	1.54	0.40	2.82	-1.30	0.30	-0.4	1.23	0.0
Diluent 3	3f Trifunctional acrylate	0.57	-6.20	4.78	-5.90	2.77	-10.7	0.59	-5.8
Diluent 4	2f Cyclic diacrylate	0.73	1.00	3.23	0.10	1.05	-10.8	0.47	-0.6
Diluent 5	2f Difunctional acrylate	1.41	-5.10	5.43	0.30	1.76	-6.7	1.53	-5.8

Table 7. Adhesion / Delamination of Oligomer Blends

Resin ID	Description	Modulus (kpsi)	Elong-ation (%)	Dry Heat	Damp Heat	Thermal Cycling	Humidity Freeze
ALUA 1	6f Aliphatic UA	468.0	1	Fail	Fail	Fail	Fail
ALUA 2	6f Aliphatic UA (polyether)	175.7	9	Pass	Pass	Fail	Fail
ALUA 3	4f Aliphatic UA (poly caprolactone)	167.8	7	Fail	Fail	Fail	Pass
ALUA 4	2f Aliphatic UA (polyester)	12.8	28	Pass	Pass	Pass	Pass
ALUA 5	2f Aliphatic UA (poly caprolactone)	67.2	33	Pass	Pass	Pass	Pass
ALUA 6	2f Aliphatic UA (polyester)	185.6	12	Pass	Pass	Fail	Fail
ARUA 1	2f Aromatic UA (polyether)	20.8	20	Pass	Pass	Pass	Pass
EA 1	2f Modified EA	13.7	20	Pass	Fail	Pass	Pass
EA 2	2f Modified EA	231.8	7	Pass	Fail	Fail	Fail
PEA 1	3f PEA	21.0	16	Pass	Pass	Fail	Pass

Table 8. Adhesion / Delamination of Diluent Blends

Diluent ID	Description	Modulus (kpsi)	Elong-ation (%)	Dry Heat	Damp Heat	Thermal Cycling	Humidity Freeze
Diluent 1	1f Acidic acrylate	114.0	92	Pass	Pass	Pass	Pass
Diluent 2	1f Urethane acrylate	5.7	103	Pass	Pass	Pass	Pass
Diluent 3	3f Trifunctional acrylate	355.5	2	Fail	Pass	Fail	Fail
Diluent 4	2f Cyclic diacrylate	244.7	4	Pass	Pass	Pass	Pass
Diluent 5	2f Difunctional acrylate	185.5	12	Pass	Pass	Fail	Fail

Table 9. QUV Exposure (2000 hours) of Oligomer Blends - Optical Results

Resin ID	Description	Functionality	Δ E	Δ %T	Visual Appearance
ALUA 1	Aliphatic UA	6	1.85	2.40	Clear, slightly yellow, with cracks
ALUA 2	Aliphatic UA (polyether)	6	0.98	0.10	Clear, colorless
ALUA 3	Aliphatic UA (poly caprolactone)	4	1.26	0.40	Clear, colorless
ALUA 4	Aliphatic UA (polyester)	2	0.97	0.60	Clear, colorless
ALUA 5	Aliphatic UA (poly caprolactone)	2	1.05	0.70	Clear, colorless
ALUA 6	Aliphatic UA (polyester)	2	2.35	1.30	Clear, slightly yellow
ARUA 1	Aromatic UA (polyether)	2	19.74	-3.40	Clear, very yellow
EA 1	Modified EA	2	17.43	-5.80	Clear, very yellow
EA 2	Modified EA	2	8.33	0.80	Clear, yellow
PEA 1	PEA	3	18.37	-2.80	Clear, very yellow

Table 10. QUV Exposure (2000 hours) of Diluent Blends - Optical Results

Diluent ID	Description	Functionality	Δ E	Δ %T	Appearance
Diluent 1	Acidic acrylate	1	3.85	0.10	Clear, yellow
Diluent 2	Urethane acrylate	1	0.67	0.90	Clear, colorless
Diluent 3	Trifunctional acrylate	3	0.90	0.80	Clear, colorless
Diluent 4	Cyclic diacrylate	2	0.59	0.80	Clear, colorless
Diluent 5	Difunctional acrylate	2	2.35	1.30	Clear, slightly yellow

[i] [i]IEC 61646, “Thin-film terrestrial photovoltaic (PV) modules – Design qualification and type approval, edition 2.0, 2008-05.