High Performance UV-curable Coatings for Different Metal Substrates

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Abstract

Improving adhesion, temperature stability, and toughness of UV-curable coatings on metals remain one of the major issues for industrial application. Types of oligomers and monomers are major determinants of these final properties of UV curable coatings. In this study UV-curable coatings were obtained from different types of oligomers: Novolac epoxy acrylate, Bisphenol A based epoxy acrylates, acrylic acrylate, aromatic urethane acrylate, and aliphatic polyether or polyester based polyurethane acrylates. Coatings were evaluated over different flat metal substrates and wires. Physical-mechanical properties of UV cured coatings, as well as their low and high temperature stability were investigated. Coatings having good adhesion to copper, stainless steel, aluminum and zinc–galvanized steel are discussed. Adhesion dependence on time, curing conditions and substrate cleaning is shown.

Introduction

UV-curable coatings for different metal substrates are used in a wide range of applications in coil coatings, automotive, and metal industry for refinish application. UV curable coatings on metal exhibit a wide range of toughness, hardness and chemical resistance. The necessary properties of the coating are determined by their intended use. For example, extreme temperature performance is required for coatings used on superconductor tapes[1, 2]. Such coatings require stability in liquid nitrogen or liquid helium (operating temperatures for high temperature and low temperature superconductors), as well as extreme high temperature for special applications (for example, 200°C for several hours). On the other hand, coatings for coil need to have high elongation in order to withstand all the bending and winding tests. Additionally, coatings with higher elongation are usually needed for improvement of adhesion and low temperature performance, while high crosslink density is needed to increase the thermal stability and modulus of a coating with simultaneous decrease in elongation and adhesion [3, 4].

Achieving high flexibility, low and high temperature stability, and good adhesion at the same time is a challenging process. It is known that while monofunctional monomers increase elongation and flexibility of the coatings, multifunctional monomers increase hardness, chemical resistance and thermal stability. The traditional approach for achieving the required properties is that formulators employ a combination of monofunctional and multifunctional monomers with different functionalities. For those coatings where the most important requirements are elongation and adhesion, the addition of multifunctional monomers may adversely affect these properties. Therefore, avoidance of multifunctional monomers may provide the theoretical advantage for the achievement of the best elongation and adhesion properties.

The first aim of this study was to test if formulations of monofunctional monomers with different classes of oligomers could obtain the best combination of properties necessary for the insulation of superconductor tapes and wires. The second aim was to study adhesion to different substrates and dependence of adhesion on cure conditions and substrate cleaning.

Experimental

Viscosity measurements were conducted on a Physica MC-10 viscometer, at 25°C, using the Z3 system and a shear rate of 50 sec^{-1}. Formulations were applied to Mylar as 3 mil films and cured under nitrogen, at 1 J/cm^2. Physical-mechanical properties were checked after 16-24 hrs conditioning, in controlled environment, using an Instron. Thermal stability was studied by evaluating the weight loss, after 6 hrs, in a 205° C oven. Materials which had the best thermal stability, and high elongation (>60%) were applied to the superconductor tape and checked for 100 cycles of 30 min in liquid nitrogen followed by 30 min in room temperature air.

Coatings on flat metal substrates were drawn down, using a one mil bird bar applicator, on acetone-wiped panels, and cured at 1 J/cm^2, with Fusion 300 W/in D lamp, in nitrogen, unless otherwise indicated. A comparison of the coating's properties at different cure conditions was done with a 300 W/inch and 600 W/inch Fusion D-lamps. Doses were measured with Light Bugs IL390B and IL 390C, respectively. Cross-hatch adhesion was tested according to ASTM method D3359 using Permacel tape and a Gardner 8-blade scratcher. Reacted acrylic units (%RAU) were evaluated using Fourier Transform Infrared Spectrophotometry (FTIR). Strip force of the coating from the wire was measured according to Fiber Optic Testing Procedure FOTP-178. Dielectric breakdown voltage and dielectric strength were evaluated by Plastic Technology Lab. Incorporated.

Results and Discussions

Commercial oligomers obtained from Sartomer, Cytec and Bomar were investigated in order to find the best combination of physical-mechanical properties: high elongation and high modulus. Several monofunctional monomers were compared in formulations with urethane acrylate. Subsequently, several oligomers were formulated using the most favorable monomer.

The formulations based on 70% of polyether urethane acrylate 1 (PEUA-1), and 24% of monofunctional monomer dimethyl acrylamide - (DMAA), phenoxy-ethyl acrylate - (PEA) or cyclic trimethylolpropane formal acrylate - (CFTA) were tested. The remaining 6% of the formula were photoinitiators and adhesion promoter (Figure 1).

Figure 2 demonstrates that DMAA provides the best combination of high modulus and high elongation. A similar formulation with DMAA based on polyether urethane acrylate 2 (PEUA-2), with higher molecular weight, was tested for the influence of HDDA as co-monomer added at 5, 10, and 15 % levels. Film with no HDDA added had higher elongation and lower modulus than the film based on lower molecular weight PEUA-1. As predicted, addition of HDDA decreased elongation and increased modulus.

It was important to find an oligomer which would give high elongation and high modulus together with high temperature stability. Several types of oligomers were tested in formulations with DMAA (Table 1): Novolac epoxy acrylate, low and high viscosity Bisphenol A based epoxy acrylates, acrylic acrylate, two aliphatic polyether based polyurethane acrylates (PEUA-1 and PEUA-2) and aromatic urethane acrylate (ArUA). All the formulations contained 70% of oligomer, 20% of monomer and 10% of the mixture of acidic adhesion promoter, antioxidant, and photoinitiators.

Figure 1. Influence of monofunctional monomers on physical-mechanical properties

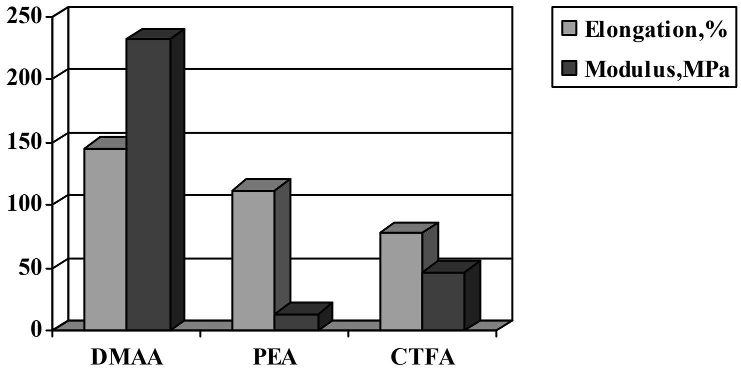

Figure 2. Influence of HDDA (%) on mechanical properties of aliphatic polyether urethane acrylate 2/ DMAA formulation

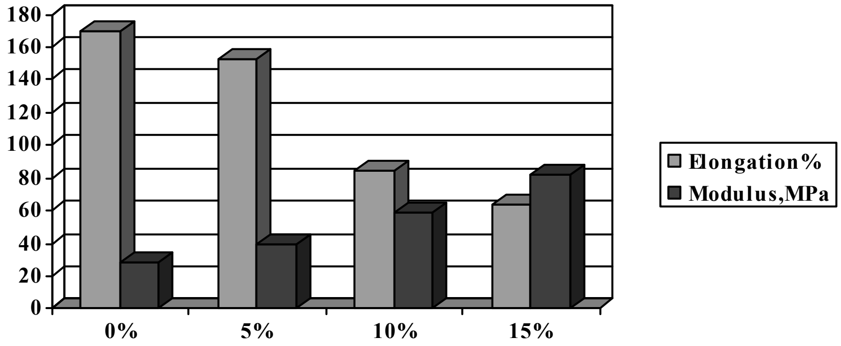

Table 1. Physical-mechanical properties of formulations based on different oligomers.

	Novolac epoxy acrylate	Epoxy acrylate-1	Epoxy acrylate-2	Acrylic acrylate	PEUA-1	PEUA-2	ArUA
Viscosity, mPa·s	1440	180	865	940	8680	6100	895
Tensile , MPa	39	40	43	brittle	23	10	7
Elongation, %	3	3	5		143	170	63
Modulus, MPa	1600	1412	1357		250	29	60
Wt loss, % after 6 hrs at 205°C	14	13	11	17	17	25	23

Table 1 shows that a wide range of viscosities was covered. Epoxy acrylates gave materials with high modulus and low elongation. Acrylic acrylate films were so brittle that it was impossible to measure their physical-mechanical properties. Polyether urethane acrylates had high elongation but undesirable high weight loss at 205°C. Aromatic urethane acrylate exhibited low modulus and high weight loss similar to PEUA-2.

Due to the fact that polyesters are more thermally stable than polyethers, it was necessary to investigate several polyester urethane acrylates and polyester acrylates in order to find the required combination of the properties. Difunctional aliphatic polyurethane ester acrylate (PUEsterA-1), aliphatic polyurethane ester acrylate (PUEsterA-2), polyester acrylate (PEsterA), and multifunctional polyester acrylate (PEsterA-m) were investigated and compared. In order to improve weight loss, the amount of photoinitiators that could give rise to volatiles at high temperature was decreased to 2%. The oligomer / monomer ratio was 70 / 24.5. The antioxidant and acidic adhesion promoter concentrations were kept constant for all the formulations.

The physical-mechanical properties of these formulations, their weight loss at 205°C, and adhesion of 1 mil films to different metal substrates are shown in Table 2. Adhesion was checked both 1 hr and 24 hrs after cure. It was demonstrated, that all polyester based acrylates showed better properties than other formulations tested previously. The best combination of physical-mechanical properties, high thermal stability and adhesion was obtained with polyester aliphatic urethane acrylate (PUEsterA-1). Additionally, for all polyester based difunctional oligomers, relatively high elongation and high modulus values could be achieved in formulations with DMAA. Multifunctional polyester acrylate exhibited low elongation and high modulus. Relatively low weight loss (6-9%) is achievable for polyester based urethane acrylates or polyester acrylate oligomers. As anticipated, adhesion strongly correlated with elongation. Improvement of adhesion at 24 hours could be explained by the process of polymeric network relaxation.

Table 2. Comparison of the properties of formulations based on different oligomers.

Properties	PUEsterA-1	PUEsterA-2	PEsterA	PEsterA-m
Viscosity, mPa·s	2490	3900	1145	57
Tensile , MPa	26	24	35	22
Elongation,%	68	35	30	3
Modulus, MPa	860	735	1624	1005
Wt loss, % after 6 hrs at 205°C	6.8	7.9	9.3	5.9
Adhesion, % to aluminum 1hr/24hr	100/100	90/100	90/100	10/10.
Adhesion, % to copper (1hr/24hr)	95/100	100/100	90/100	0/90
Adhesion, % to steel (1hr/24hr)	95/100	20/100	20/40	0/90

In order to find out if any monofunctional dimethyl acrylamide analogs or other relatively high Tg monomers could be used, a DMAA based formulation was compared against similar formulations with different monomers used in combination with PUEsterA-1. Data are presented in Table 3. It is shown that only DMAA worked as a good diluent, while other monomers led to high viscosity and formulations were required to be applied at 50-60° C.

Table 3. Comparison of monofunctional monomers.

	DMAA	N-isopropyl acryl amide	Diacetone acryl amide	IBOA	N-vinyl caprolactam
Viscosity, mPa·s	2490	35200*	26290	26530	16340
Tensile , MPa	26	36	28	29	37
Elongation,%	68	102	88	88	83
Modulus, MPa	860	875	611	682	777
Wt loss,% after 6 hrs at 205°C	6.8	8.1	21.8	14.4	8.1
Adhesion, % to aluminum	100/100	50/95	40/100	95/100	0/0
Adhesion, % to copper	95/100	0/100	0/0	0/100	0/0
Adhesion, % to steel	95/100	0/0	30/100	0/100	0/0

Importantly, all the films possessed good physical-mechanical properties. DMAA, N-isopropyl acryl amide and N-vinyl caprolactam afforded good thermal stability, while IBOA and diacetone acryl amide showed high weight loss. DMAA based coatings showed quick development of adhesion, while other monomers were developing adhesion to some substrates only after 24 hrs. Interestingly, for N-vinyl caprolactam based formulations adhesion to tested substrates was not achieved, despite having the perfect combination of physical-mechanical and thermal characteristics.

Table 4 shows that in order to achieve good adhesion to aluminum, stainless steel or non-oxidized printed circuit board copper while curing in air, cleaning with acetone was necessary. Cleaning with COMET cleanser or other degreasing, slightly abrasive material was needed for copper alloy as rolled (Metaspec) CA-110, ETP. As demonstrated in Tables 2 and 3, Table 4 also shows that prolonged time is needed for development of high adhesion. As mentioned previously, relaxation of the polymeric network may be responsible for the increased time for improved adhesion. Slightly worse adhesion was obtained while curing in nitrogen. It might be explained by a better through-cure in the absence of air inhibition and obtaining higher-modulus and more rigid films.

In order to check this hypothesis, the modulus of this formulation was checked in air and nitrogen at different cure doses for different lamps intensities. The results presented in Figure 3 show a modulus increase with cure dose and a small increase in the modulus of coatings obtained in nitrogen versus air, using 3 mil films. This difference could be more significant for coatings with only a 1 mil thickness. It is interesting to note that higher modulus coatings were obtained with a cure under a 300 W/inch lamp versus a 600 W/inch lamp. Obviously a higher initiation rate from a higher intensity lamp led also to an increase of termination rate and formation of more brittle, shorter chain polymeric network. At the same time, complete reaction of acrylic double bonds was observed.

Table 4. Dependence of PUEsterA-1 best coating adhesion on time and cleaning of the substrate

Substrate	atmosphere	Testing time	Metal substrate cleaning method	
			Acetone	Comet
Stainless steel, matte finish	Air	1 hr	100	
		24 hr	100	
	nitrogen	1 hr	15	100
		24 hr	100	100
Cold rolled steel unpolished from ACT lab	Air	15 min	100	100
		3 hrs	100	100
	nitrogen	15 min	98	100
		3 hrs	96	100
Zink galvanized steel unpolished (ACT lab) ACT E60 EZG 60G	Air	1 hr	100	
		24 hr	100	
	nitrogen	1 hr	100	
		24 hr	100	
copper clad laminate	air	1 hr	100	
		24 hr	100	
	nitrogen	1 hr	100	
		24 hr	100	
copper alloy as rolled CA-110, ETP (Metaspec)	air	1 hr	0	55
		24 hr	0	100
	nitrogen	1 hr	0	65
		24 hr	0	100

Comparison of RAU% for 3 mil films cured with different lamps at different doses, showed practically complete reaction of acrylic double bonds on the top and the bottom of the films. Small decrease of oligomer RAU% is observed in films cured at 400 mJ /cm^2, and it is more pronounced for a 600 W/inch lamp (Table 5).

Good correlation between %RAU of 1 mil cured wire coatings and their adhesion was found during experiments on the Draw Tower Simulator. PUEsterA-1 formulation was applied through the die on a stainless steel wire and cured with a 600 W/inch lamp at various line speeds. Table 6 shows the decrease of strip force with increase of a line speed that could be explained with lower degree of cure generally, and especially with lower conversion of double bonds of the bottom layer of the coating. Similar results were achieved for these coatings obtained on a copper wire. Good adhesion, flexibility and stability in liquid nitrogen were observed.

Figure 3. Modulus change with a dose, lamp intensity and cure atmosphere.

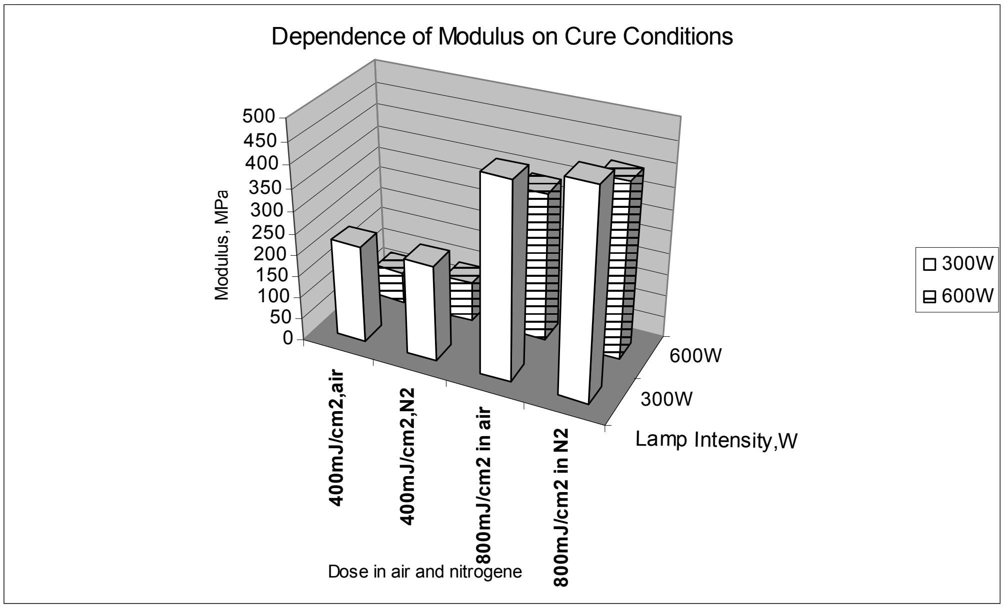

Table 5. %RAU for 3 mil films based on PUEsterA-1 formulation.

Speed, m/min	Fusion lamp	Dose, mJ/cm^2	Monomer %RAU (795cm^{-1})		Oligomer %RAU (810cm^{-1})	
			Top	Bottom	Top	Bottom
7.98	300 W/inch	1000	99.6	99.4	100	100
9.6		800	99.9	99.8	99.5	97.8
19.2		400	99.2	98.8	99.3	94.5
13.4	600 W/inch	1000	100	98.9	100	100
16.8		800	99.8	99.6	99.8	98.1
31.3		400	99.4	98	97.5	88.6

Table 6. %RAU on stainless steel wire for films based on PUEsterA-1.

Speed, m/min	600W/ inch Power,%	Monomer %RAU		Oligomer %RAU		Strip force,g	Adhesion to stainless steel wire
		Top	Bottom	Top	Bottom		
50	67	99	99.6	100	100	717	Impossible remove with nails, but possible with a scissors
100	67	96.9	99	99.2	97.7	663	
200	67	96	93.4	100	75.7	620	Difficult, but could be removed with nails
250	100					502	Possible to remove with nails
400	100					288	Easy to remove
500	100					259	

Dielectric strength of the best formulation is pretty high and considered to be adequate for a wire insulation material. It is important, that the dielectric strength did not change after 6 hrs, in 205°C oven (Table 7). This could be important for the use of insulation coating at high temperature.

Table 7. Dielectric strength before and after 6 hrs in the oven at 205°C.

Formulation	Thickness, mil	Breakdown voltage, V	Dielectric strength(V/mil)
PUEsterA-1 formulation	3	6.9	2170
PUEsterA-1 formulation after 6 hrs in 205°C oven	3	6.4	2140

Adhesion to copper and stainless steel of this formulation, and its low viscosity (LV) analog was compared with adhesion of other materials (epoxy-acrylate based and polyether –urethane based, formulated with mixture of monofunctional monomers and small addition of trifunctional monomer. Adhesion at ambient conditions and after 10 cycles (room temperature –liquid nitrogen) was checked (Table 8). It was shown that polyester urethane aliphatic acrylate diluted with monofunctional dimethyl acrylamide had the best adhesion for both metals and withstood low temperature cycling.

Table 8. Adhesion of different coatings to copper and stainless steel

	Adhesion, % to copper	Adhesion,% to copper after cycling	Adhesion % to stainless steel	Adhesion % to stainless steel after cycling
PEUA-1	80	85	85	95
PEUA-2	0	0	0	0
PEUA-2 (LV)	*50*	*50*	95	100
PEUA-3	*65*	*90*	50	50
Epoxy-acrylate based-1	*87*	*85*	80	80
Epoxy-acrylate based-2	30	40	40	40
Epoxy-acrylate based-3	98	0	30	0
PUEsterA-1	**98**	**100**	**100**	**100**
PUEsterA-1 (LV)	**96**	**100**	**100**	**100**

Conclusions

It was shown that polyester based aliphatic urethanes can be formulated with monofunctional dimethyl acrylamide to achieve high elongation, high modulus coatings, and excellent low and high temperature stability. They can also be cured with high speed in air and withstand high temperature without losing dielectric strength. Good adhesion to several metal substrates at ambient conditions and no change of adhesion with liquid nitrogen and room temperature cycling was demonstrated.

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