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Technical bulletin

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Energy-efficient insulative coatings for battery cell applications

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Energy-efficient insulative coatings for battery cell applications

ABSTRACT

In response to the global shift toward electric vehicles (EVs) in the next decade, automotive manufacturers worldwide are intensifying their focus on EV production. This surge in EV adoption has created a demand for enhanced performance in battery-related coatings. Among the solutions gaining traction, UV-curable coatings have garnered significant attention from manufacturers due to their rapid curing rate, minimal energy consumption, and ease of application processes. These qualities are pivotal for achieving heightened industrial efficiency and enabling large-scale production. Notably, sprayable UV-cured coatings with low volatile organic compounds (VOCs) and a 100% solid composition are emerging as a viable alternative to traditional PET films. They offer comparable dielectric protection while having thinner profiles and eliminating the risk of delamination. Within this context, Arkema is positioned to showcase its cutting-edge UV-curable acrylate resins, empowering formulators to address the multifaceted challenges of this application. These products offer outstanding dielectric properties, superior adhesion, flexibility, and seamless assembly capabilities, further reinforcing the EV industry's pursuit of advanced battery coatings.

INTRODUCTION

The surge in demand for electric vehicles (EVs) has spurred automotive manufacturers to intensify their focus on improving battery performance, leading to significant advancements in battery-related coatings. Among these coatings, energy-efficient and effective insulative coatings play a vital role in ensuring the longevity and safety of battery cells. UV-curable coatings have emerged as a promising solution due to their fast-curing rate, low energy consumption, and ease of application. As the automotive industry shifts towards EVs, there is a critical need for coatings that not only offer excellent dielectric protection but also enhance properties such as durability, adhesion, and flexibility. While traditional coatings like PET films have been widely utilized, concerns over delamination and environmental impact are prompting a reassessment[1]. In this context, sprayable UV-cured coatings with low volatile organic compounds (VOCs) and a solid composition are gaining momentum as a viable alternative. These coatings provide comparable dielectric protection to conventional methods while offering thinner profiles and mitigating the risk of delamination. However, to fully leverage the advantages of UV-curable coatings, the selection of optimal oligomers is crucial. This paper underscores the importance of utilizing optimal components in UV-curable coatings for battery cell applications and it explores how these coatings contribute to enhancing energy efficiency, durability, and overall performance in EV batteries, thereby propelling the advancement of the electric vehicle industry.

EXPERIMENTAL SETUP AND MEASUREMENT TECHNIQUES

The film samples consisted of carefully selected optimal oligomers, monomers, photoinitiators, and additives or fillers. Initially, a mixture of fillers and an oligomer was introduced into a Flacktek® polypropylene high-speed mixer cup and blended for 2 minutes at 2000 rpm. Subsequently, the blended sample underwent milling using three roll mills until achieving a uniform dispersion of all additives within the oligomer. Following the milling process, the sample underwent quality assessment for dispersion using a Hegman grind gauge (0-25 µm). Finally, the remaining components were integrated into the milled sample, and the mixture underwent further blending for 2 minutes at 2000 rpm using a high-speed mixer. The resulting blended resin, applied onto aluminum substrates, was cleaned with toluene followed by an acetone wipe prior to coating, achieving a thickness of 60 µm using a drawdown bar. Subsequently, the films were cured using both an LED light (395 nm) and a fusion lamp (H bulb). Coated specimens were subjected to aging in both an environmental chamber at 85°C/85% RH and through electrolyte soaking for up to 4 weeks. Testing on these aged samples was conducted immediately after the aging tests. The coated specimens that had been immersed in electrolyte solvents were dried using cleanroom wipes and alcohol prior to testing. The properties of the cured samples were evaluated as follows:

- **Flexibility:** A conical mandrel test instrument, in compliance with ASTM D522, was employed to evaluate the flexibility of the coatings. The bend tester features a bending lever equipped with a roller that pivots on a steel conical mandrel, offering bend angles of 90 and 180 degrees, and with a diameter ranging from 4 mm to 34 mm. Using the lever, the coated substrate was bent over the conical cone. Subsequently, each sample underwent examination for cracks or crazing.

- **Adhesion**: The adhesion of the coated resins to the aluminum plate was assessed following ASTM Standard D3359 using a crosshatch test. This test involved using a blade to create small squares on the surface of the coatings, with six cuts made in the coating during the first pass, followed by a second pass at 90° to form a square lattice pattern. A transparent tape was then applied over the patterned surface and swiftly removed to determine the amount of coating lifted off by the test tape. The adhesion strength of the crosshatch was rated on a scale from 0 to 5, with 5 representing the highest adhesion strength, as outlined in the ASTM standard.

- **Pencil hardness:** Graphite pencils of varying hardness are utilized to assess the hardness of a coating surface in accordance with ASTM D3363-05. The softest pencil capable of producing a scratch on the coating surface establishes its hardness relative to graphite pencils.

- **Flexural Modulus (ASTM D790):** Flexural modulus was measured using a three-point bend test on an Instron® Dual Column Table Frame Model No. 5966. Samples were cured in silicone molds of specific dimension (80 mm x 10 mm x 4 mm) under 395 nm LED light using a Phoseon LED lamp at 30 fpm, intensity of 10, three passes each side. The cured parts were placed in the constant temperature room (23°C +/-2°C, 50% +/-10% RH, in line with ASTM D618) 24 hours prior to testing. Data was reported as an average of at least three samples.

- **Breakdown strength:** The breakdown strength of cured films was determined following ASTM D-149 standard, with a ramp rate of 500 V/s. This test involved employing a 6.35 mm stainless steel ball on a brass substrate immersed in 25ºC silicone oil to reduce electric field non-uniformity and minimize the likelihood of a film defect being present at the test location. The thickness of the cured film was measured and recorded at each breakdown location before the occurrence of breakdown. Twenty measurements were taken on each film, and the dataset was analyzed using a 2-parameter Weibull distribution with a 95% confidence interval.

- **Volume Resistivity:** To ascertain volume resistivity, the thickness of the cured samples was initially determined using a Heidenhain Metro length gauge unit, which provides accuracy within ± 0.2 m and has a measuring range of 0 to 12 mm. Five different points within a 1.0 cm^2 area of coated samples on aluminum substrate were selected for film thickness measurement, and their average value was used for calculating the volume resistivity. Volume resistivity was assessed following ASTM D-257 standard using a Keithley 6517B and 8009 fixture at room temperature. Prior to measurement, an alternating polarity of 500 V was applied to the cured film for 60 seconds with a 2 nA current range to ensure a net zero charge.

RESULTS AND DISCUSSION

Table 1 illustrates the significance of utilizing optimal oligomers for battery coating applications. Upon comparing the data from Table 1, it becomes apparent that incorporating a flexibilizer into the resin formulation yields improvements across various properties. Specifically, the resistivity values at 500 V – 60 s show a slight increase with the addition of the flexibilizer, suggesting potentially enhanced electrical insulation properties. Furthermore, the inclusion of the flexibilizer maintains or enhances adhesion and pencil hardness scores, indicating improved bonding and surface durability. Notably, the results of the mandrel bend test demonstrate significantly enhanced flexibility for resin formulations containing the flexibilizer, as evidenced by lower diameter range values, signifying a greater ability to withstand bending without experiencing cracking or damage. This underscores the positive contribution of the flexibilizer to both electrical and mechanical properties, rendering it a valuable addition to the resin formulation for battery coating applications where flexibility is a key consideration.

Film coated on Al substrate	Ave volume resistivity (Ω*cm) 500 V - 60 s	Standard deviation (Ω*cm)	Adhesion	Hardness	Flexibility Mandrel bend test 90° Diameter range 4-34 mm
Resin formulated without flexibilizer					
30 µm – one layer	1.47E+13	6.4E+12	2	3H	Passed > 18 mm
60 µm – one layer	2.60E+13	1.6E+13	4	4H	Not passed
60 µm – two layers	2.77E+13	1.7E+13	5	5H	Not passed
Resin formulated with flexibilizer					
30 µm – one layer	1.83E+13	7.3E+12	5	3H	Passed
60 µm – one layer	1.86E+13	8.3E+12	5	4H	Passed > 6 mm
60 µm - two layers	2.25E+13	9.3E+12	5	7H	Passed > 6 mm

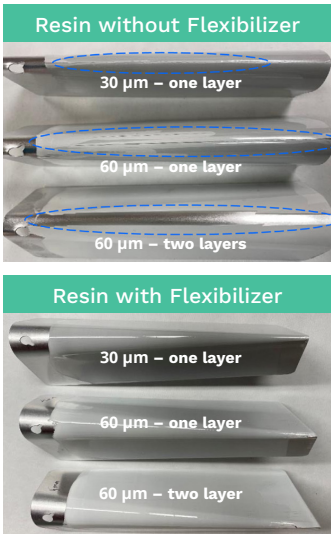

Table 1: Flexibilizer - Performance of monofunctional diluents.

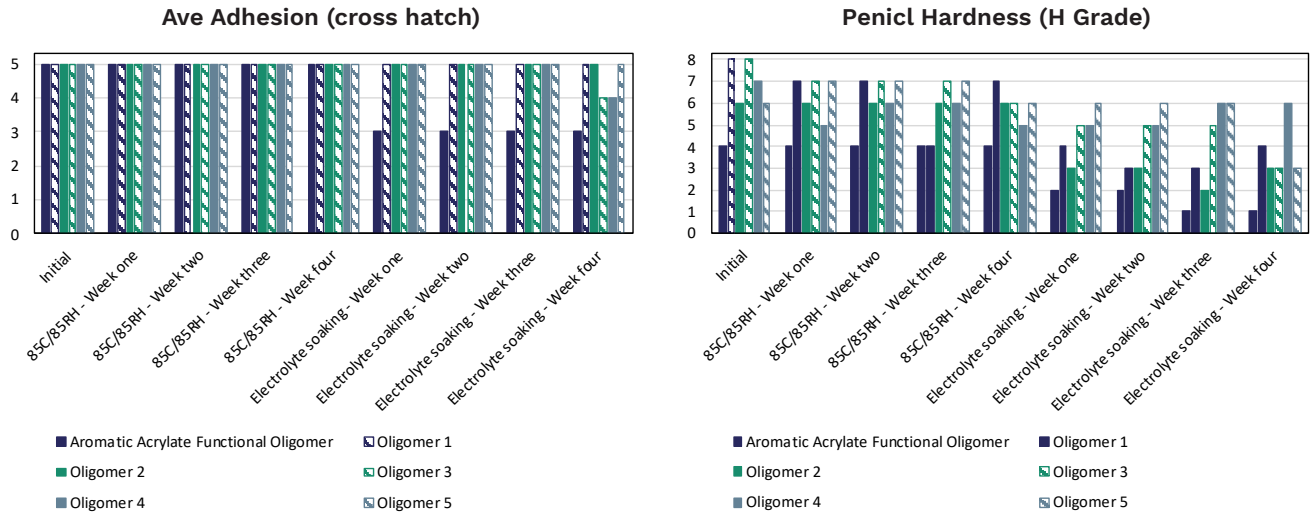

Figure 1: Evaluation of hydrophobic oligomers for battery coating applications: assessing adhesion and hardness characteristics.

Comparing the data for average adhesion and pencil hardness in Figure 1 across the provided oligomers reveals distinct trends in their performance under various aging conditions. In terms of average adhesion, all oligomers exhibit consistently high scores of 5 initially and throughout the 85°C/85% RH aging tests, suggesting excellent initial adhesion and resistance to environmental stress. However, during electrolyte soaking, slight variations emerge, particularly for aromatic acrylate functional oligomers, which exhibit lower scores compared to the initial weeks, indicating a potential decrease in adhesion over prolonged exposure to electrolytes. Conversely, in terms of pencil hardness, the performance varies across oligomers and aging conditions. Initially, Oligomer 1 demonstrates the highest hardness, while Aromatic Acrylate Functional Oligomer shows the lowest. Throughout the aging tests, most oligomers maintain relatively stable hardness levels, with some fluctuations observed, such as a decrease in hardness for Aromatic Acrylate Functional Oligomer during electrolyte soaking. However, Oligomers 2, 4, and 5 consistently exhibit higher hardness values across all conditions compared to the rest. Overall, while all oligomers display robust adhesion initially, variations in hardness performance emerge, with Oligomers 2, 4, and 5 demonstrating superior hardness properties throughout the aging tests. Thus, these urethane acrylates present a balanced mix of adhesion, hardness, and resistance to electrolytes.

Figure 2 displays the bend test results at 90 and 180 degrees for both aromatic oligomers and other oligomers. The data indicate that the other oligomers generally exhibit superior flexibility retention compared to aromatic oligomers across both aging tests at 85°C/85%RH and electrolyte soaking. Consequently, the other oligomers outperform aromatic oligomers due to their molecular structure, which provides inherent flexibility and resistance to degradation, rendering them more suitable for applications requiring sustained flexibility under harsh conditions such as battery coatings.

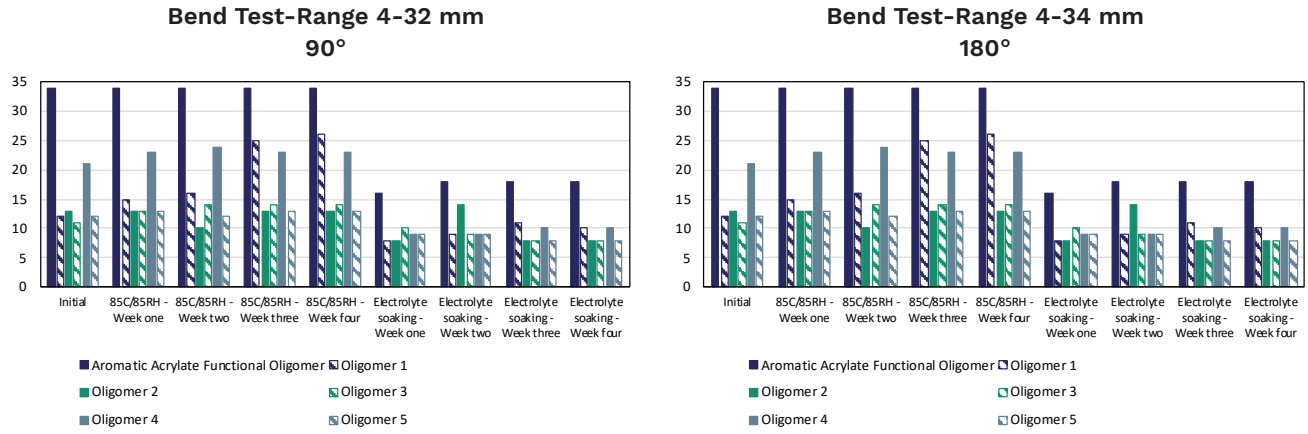

Figure 2: Comparison of flexibility among resin formulations employing various oligomers.

Based on the provided data in Figure 3, the adhesion properties across all three oligomers remain consistently high, with initial and post-electrolyte exposure measurements retaining a rating of 5, indicating excellent adhesion. However, when assessing hardness, the high viscosity acrylated epoxy oligomer exhibits the highest initial hardness at 6, while the aromatic acrylate functional oligomer and medium viscosity acrylated epoxy oligomer display slightly lower initial hardness values at 4. Moreover, after exposure to electrolyte and lithium salt at -85°C for 2 hours, there's a decrease in hardness for all three oligomers, with the high viscosity acrylated epoxy oligomer retaining the highest hardness at 5. In terms of flexibility, lower values do indeed indicate better performance. Both before and after exposure to the electrolyte and lithium salt aging test, the aromatic acrylate functional oligomer exhibited the lowest flexibility, as evidenced by cracking from 4 to 34 mm after the mandrel bend test at 90°. Following this, the medium viscosity acrylated epoxy oligomer displayed slightly improved flexibility, while the high viscosity acrylated epoxy oligomer demonstrated the best flexibility performance.

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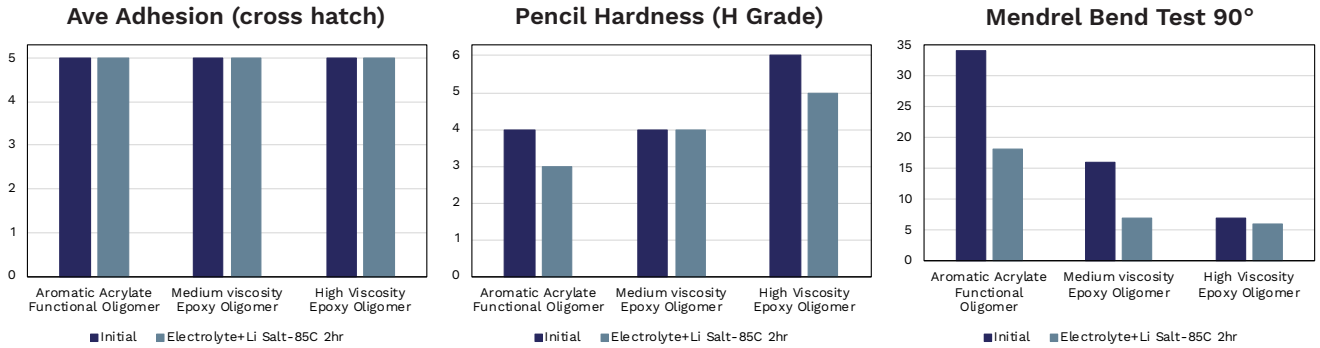

Figure 3: Assessing the adhesion, hardness, and flexibility characteristics of acrylated epoxy oligomers for battery coating applications.

After subjecting the aromatic acrylate functional oligomer, medium viscosity acrylated epoxy oligomer, and high viscosity acrylated epoxy oligomer to an electrolyte+lithium salt aging test, slight decreases were observed in both volume resistivity and breakdown strength for all materials, as shown in Figure 4. However, despite these slight changes, all results remained within satisfactory ranges for battery coating applications, indicating the continued suitability of these materials for such purposes even after undergoing the aging test.

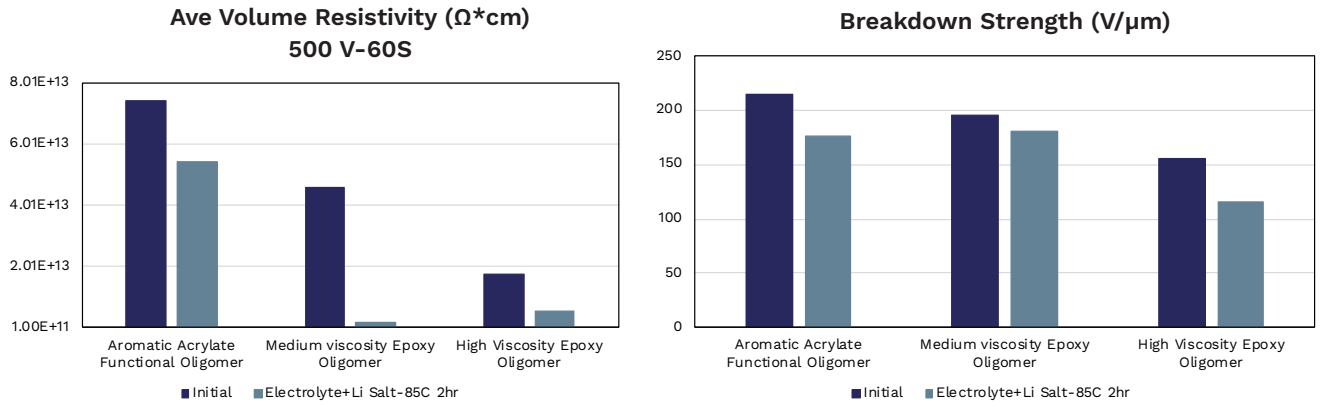

Figure 4: Dielectric performance comparison between acrylated epoxy oligomers and aromatic acrylate oligomers.

The provided data in Figure 5 presents a comparative analysis of resin formulations with different adhesion promoters and thicknesses, focusing on average volume resistivity, adhesion, and hardness properties. Commercial phosphate resin formulations consistently exhibit superior performance, showcasing higher resistivity and hardness values across various thicknesses, particularly evident in the 60 μm thickness with two layers. In contrast, silane adhesion promoters yield notably lower adhesion values and, in some cases, decreased hardness, indicating potential compromises in performance. This highlights the critical role of adhesion promoters in determining the electrical, mechanical, and adhesive properties of the resin, with phosphate adhesion promoters-based formulations emerging as the most promising choice for applications requiring robust insulation and mechanical strength.

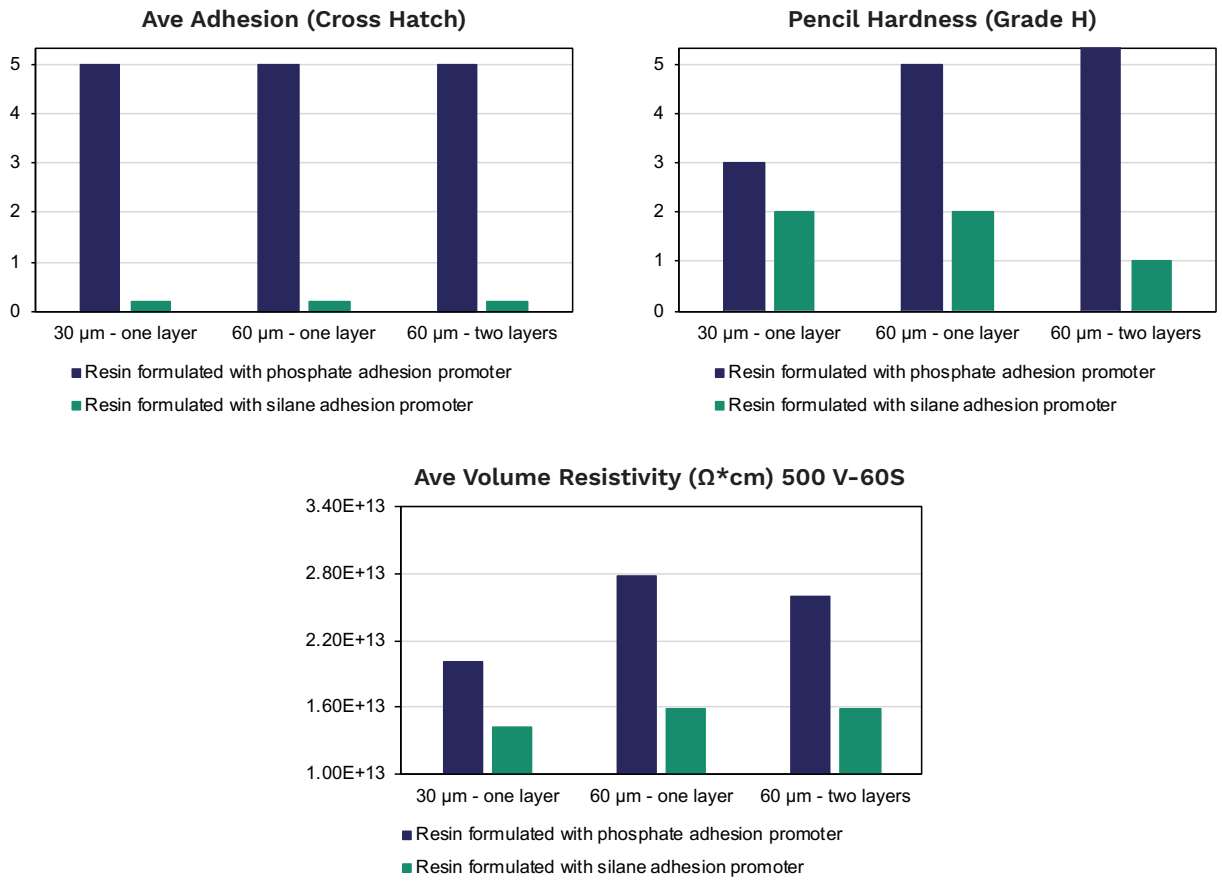

Figure 5: Comparative evaluation of resin formulations utilizing various adhesion promoters.

Comparing the results of aging tests for resin formulated with and without commercial phosphate adhesion promoters, as shown in Figures 6 and 7, both sets of data exhibit trends indicating degradation or changes in material properties over time and under specified conditions. However, the data for resin formulated without adhesion promoters generally show greater degradation, with larger decreases in volume resistivity and breakdown voltage, as well as more pronounced changes in mechanical properties such as adhesion, hardness, and flexibility. This suggests that the presence of adhesion promoters may enhance the stability and performance of the resin under aging conditions, potentially improving its electrical and mechanical properties over time. Therefore, based on the observed trends, the data for resin formulated with adhesion promoters appear to be better, as they indicate a more favorable response to aging conditions and suggest a higher level of overall performance and durability compared to resin formulated without adhesion promoters.

Figure 6: Comparison of Mechanical Properties in Cured Coated Films with and without Adhesion Promoter.

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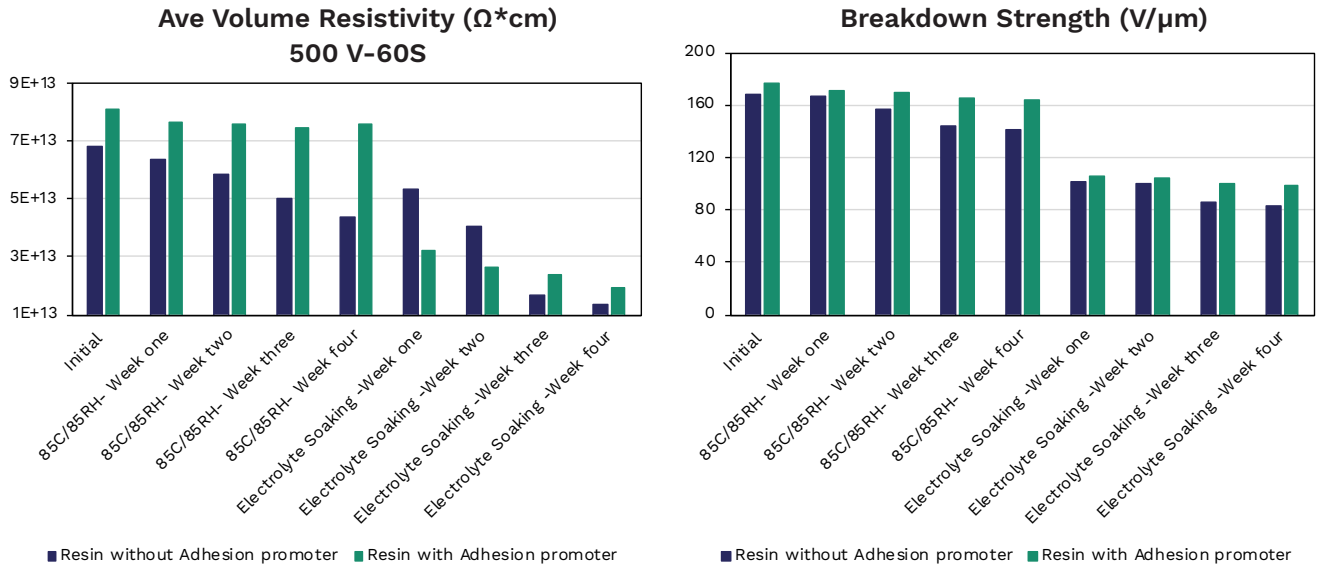

Figure 7: Comparison of Electrical Properties in Cured Coated Films with and without Adhesion Promoters.

In a separate experiment, a toughened version of difunctional acrylate monomer has been evaluated for battery coating application to improve mechanical properties of formulations. Table 2 compares the mechanical properties of difunctional acrylate monomer and its toughened version. Flexural modulus was measured using a three-point bend test on an Instron. Samples were cured in silicone molds of specific dimensions (80 mm x 10 mm x 4 mm) under 395 nm LED light using a Phoseon LED lamp at 30 fpm, with an intensity of 10, and three passes each side. The cured parts were placed in a constant temperature room (in line with ASTM D618) for a minimum of 24 hours prior to testing. Data was reported as an average of at least three samples. difunctional acrylate monomer, as the control, had a flexural modulus of 2876 MPa, while the toughened version had a flexural modulus of 1672 MPa. Flexural modulus is related to the amount of energy required to bend a material. Strain at break increased from 1.48% (Control) to 4.20% for the toughened version, indicating more flexibility in the part without sacrificing flexural strength or hardness. Hardness of a material is defined as a measure of the resistance to localized plastic deformation. Hardness was measured using a Shore D durometer. Hardness of the Control was 89D, while the hardness for the toughened version was 80D. The toughness of the material is four times greater for the toughened version (0.42J) compared to the Control (0.10J).

DIFUNCTIONAL ACRYLATE MONOMER	
Appearance	Clear liquid
Functionality	2
Viscosity @ 25°C	130 mPa.s
Flexural Strength	45.16 MPa
Strain at Break	1.48%
Energy at Break	0.10 J
Flexural Modulus	2876.90 Mpa
Hardness	89.3 D
Shelf Stability	> 6 months

TOUGHENED VERSION OF DIFUNCTIONAL ACRYLATE MONOMER	
Appearance	Clear liquid
Functionality	2
Viscosity @ 25°C	2,275 mPa.s
Flexural Strength	57.80 MPa
Strain at Break	4.20%
Energy at Break	0.42 J
Flexural Modulus	1672.70 Mpa
Hardness	80.03 D
Shelf Stability	> 6 months

Table 2: Mechanical Properties of Difunctional Acrylate Monomer and its Toughened Version

The performance of these materials was evaluated for battery insulating coating under aging tests in electrolyte, as shown in Figure 8. The comparison between difunctional acrylate monomer and its toughened version reveals significant improvements in several key properties after toughening. In terms of adhesion, both materials initially exhibit high adhesion scores, but after 168 hours of electrolyte soaking, the toughened version maintains its adhesion better than difunctional acrylate monomer. Pencil hardness also sees enhancement in the toughened version, with a shift from 4H to 5H initially and from HB to 2H after soaking, indicating greater resistance to scratches and wear. Perhaps most notably, the mandrel bend test demonstrates a remarkable improvement in flexibility and durability for the toughened version, as it passes at larger diameter ranges (>14mm initially and >4mm after soaking) compared to difunctional acrylate monomer (not passed initially and >6mm after soaking). These findings suggest that the toughened version offers enhanced performance and durability, making it a promising candidate for applications requiring superior adhesion, hardness, and mechanical flexibility, particularly in harsh environmental conditions such as prolonged exposure to electrolytes.

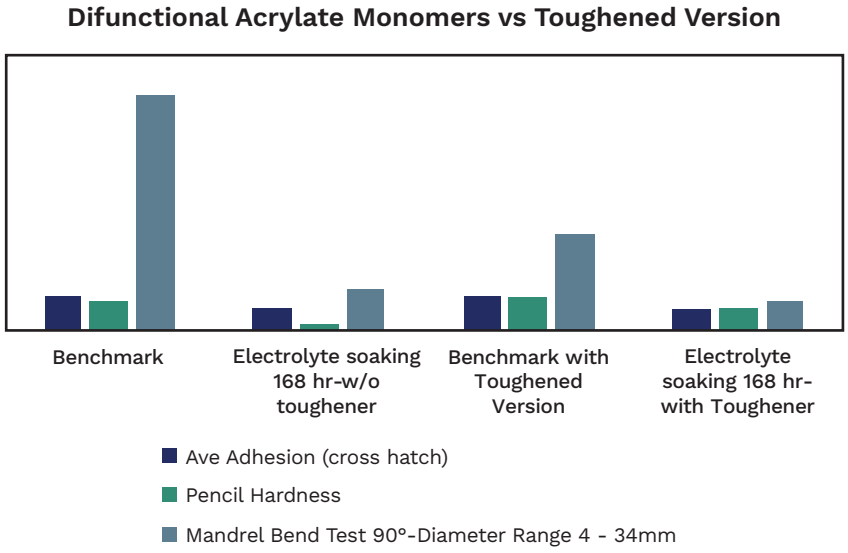

Figure 8: Toughening materials to improve flexibility and hardness.

Further evaluation has been done using the toughened version of difunctional acrylate monomer for a one-month aging test, including 85°C/85%RH and electrolyte soaking at 25°C in the presence of ethylene carbonate, dimethyl carbonate, and diethyl carbonate in a 1:1:1 ratio for insulating coating, as shown in Table 3. The results obtained from the toughened version of difunctional acrylate monomer for battery insulation coating during the aging test demonstrate consistently good performance across all properties evaluated. Over the four-week period at 85°C/85%RH conditions and electrolyte soaking, the average volume resistivity remains relatively stable, indicating the robust electrical insulation properties of the coating. Additionally, the breakdown strength consistently exceeds the required threshold, signifying excellent dielectric strength. Adhesion, assessed through cross-hatch testing, remains strong throughout, ensuring reliable bonding of the coating to the substrate. Moreover, the pencil hardness values indicate enduring surface durability. Furthermore, the flexibility test results consistently pass the criteria, highlighting the coating's ability to maintain flexibility and resist cracking even under stringent conditions. Overall, the toughened difunctional acrylate monomer formulation demonstrates commendable performance in providing reliable insulation and protection for battery applications throughout the aging test.

60 µm-one layer film coated on Al substrate	Initial	85°C/85RH				Electrolyte soaking 25°C EC/DMC/DEC - (1:1:1)			
		Week one	Week two	Week three	Week four	Week one	Week two	Week three	Week four
Viscosity @ 25°C cPs	10510.90								
Ave volume resistivity (Ω*cm) 500 V-60S	5.19E+13	6.64E+14	4.00E+14	2.55E+14	1.43E+14	1.83E+13	1.67E+13	1.54E+13	1.60E+13
Standard deviation (Ω*cm)	1.20E+13	2.80E+14	1.20E+14	1.70E+14	7.4E+13	1.30E+12	6.80E+12	3.0E+12	4.9E+12
Breakdown strength (V/um)	217.87	209.45	187.31	179.13	172.02	189.33	142.09	128.77	118.12
Ave adhesion (cross hatch)	5					3			
Pencil hardness	5H					2H			
Flexibility–Mandrel bend test 90° Diameter Range 4-34 mm	Cracked 4-14 mm					Cracked 4-5 mm			

Table 3: Performance data for toughened materials.

CONCLUSION

In conclusion, as the automotive industry undergoes a significant transition towards electric vehicles (EVs), the demand for advanced battery coatings continues to escalate. Within this landscape, Arkema's UV-curable acrylate resins stand out, boasting exceptional dielectric properties, superior adhesion, flexibility, and seamless assembly capabilities, thus meeting the multifaceted challenges posed by EV battery coatings. The performance evaluation of our materials like oligomers and flexibilizers showed enhancement in both electrical insulation properties and mechanical durability, and adhesion promoters, particularly phosphate-based formulations, significantly enhance the overall performance and durability of resin formulations, as indicated by superior electrical and mechanical properties, even under aging conditions. Additionally, our toughened materials exhibit remarkable improvements in adhesion, hardness, and flexibility, making it a promising candidate for battery insulation coatings, especially in harsh environmental conditions. Overall, these findings collectively highlight the critical role of material selection and formulation design in ensuring the efficacy and longevity of battery coatings, crucial for maintaining performance and reliability in battery applications.

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