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Selection of Crosslinking Agents for Acrylic Resin Used in External Coatings for Aluminum Packaging in the Beverage Industry

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Abstract: Paints and coatings are widely used in various applications such as walls, cars, packaging, and food products. The quality of food packaging is essential due to its direct or indirect contact with food. The demand for high-quality food packaging is increasing due to the higher production and consumption rates. However, containers used in the beverage industry often face problems like scratches and abrasions during transportation. This study aimed to investigate different formulations of external coatings for beverage cans to improve their physical resistance properties and prevent corrosion and surface damage problems. The study involved reacting an acrylic resin with six different amino resins, including methylated melamine, butylated melamine, glycoluril, methylated urea, butylated urea, and benzoguanamine, in various proportions. The results of 25 formulated samples were compared based on properties such as adhesion, durability, and chemical resistance. The outcomes of the study showed significant differences among the crosslinking agents. Among all the crosslinking agents, methylated melamine showed the most favorable results in the analyses, proving effective in almost all tests.

Keywords: crosslinking agents; acrylic resins; coatings for aluminum cams

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1. Introduction

Aluminum is widely used in the beverage industry to make beer and soda cans due to its exceptional properties, such as lightness, barrier properties, and recyclability. However, uncoated aluminum cans can be scratched, dented, and corroded. Coatings are therefore applied to the aluminum surface to prevent corrosion, providing a protective layer and improving the overall appearance.

The coating is made up of resins, solvents, and additives. Manufacturers select coatings that balance corrosion resistance, chemical resistance, heat resistance, and decorative options to suit the specific needs of the packaged beverage. Each coating type has advantages and disadvantages, making them suitable for different beverages and processing requirements. Epoxy resins based on bisphenol A diglycidyl ether (BADGE) have been commonly used to coat both the interior and exterior surfaces of aluminum cans due to their exceptional mechanical properties, excellent corrosion resistance, and strong adhesion to aluminum. However, they are prone to cracking when exposed to high temperatures and may not be suitable for some acidic beverages. As a result, these coatings are commonly used for non-acidic beverages like beer and energy drinks. Recently, other types of coatings based on different chemistries have been preferred due to concerns about the potential negative impact on human health resulting from the endocrine-disrupting properties of bisphenol A (BPA). Some examples of these alternative resins include polyester, vinyl, and acrylic [1]. The details of each type of coating are explained next [2].

Polyester coatings have good chemical resistance and offer decorative options such as metallic finishes. They can withstand pasteurization temperatures but may not provide the same level of corrosion resistance as epoxy coatings and have limited heat resistance. These coatings are suitable for non-acidic or mildly acidic beverages.

Vinyl coatings are highly flexible and offer good resistance to impact and abrasion, making them ideal for interior and exterior surfaces. However, they have limited chemical resistance and may not provide the same level of corrosion resistance as epoxy coatings. They are often used for non-carbonated beverage packaging.

Acrylic coatings have excellent moisture and gas barrier properties and a clear, glossy finish [3]. They can be formulated to be BPA-free and are suitable for non-acidic beverages. However, they have limited heat resistance and may not provide the same level of corrosion resistance as epoxy coatings. They also have been used for decorative purposes [4].

Advancements in coating technologies, such as water-based coatings, aim to minimize any environmental impacts by reducing reliance on solvent-based coatings [5]. Water-based coatings, primarily made of acrylic resin, have become eco-friendly. Acrylic resin thermosets are rigid polymers formed by a network with many properties due to the high crosslinking [6,7]. They are used in solution in varnishes, aluminum paints, and several other finishes [8].

A crosslinking agent must be incorporated into the varnish formula to achieve the chemical and physical resistance needed in the market. Crosslinking is possible through comonomers with reactive groups [9–11]. Amide, amine, carboxyl, hydroxyl, and glycidyl are the main functional groups [7,12] that allow crosslinking of the polymer scaffold with itself or other crosslinking agents. These products can be crosslinked with carboxyl (epoxy resins, oxirantriazines), hydroxyl (amine-formaldehyde resins, isocyanates), and amine (epoxy resins, isocyanates, aldehydes, amine-formaldehyde resins) [13].

Studies have demonstrated that using amino crosslinkers can boost the adhesion of acrylic resin coatings to various surfaces, resulting in superior coating durability and strength. Amino crosslinkers allow acrylic resin coatings to be more flexible, which helps them withstand substrate movements and reduces the risk of cracking or delamination. Additionally, using amino crosslinkers can accelerate the curing process of acrylic resin coatings, resulting in shorter production cycles and greater manufacturing efficiency. These crosslinkers have several other benefits, including gloss retention and improving the mechanical properties of acrylic resin coatings, such as hardness, scratch resistance, and impact resistance. They also provide flexibility in formulating coatings with diverse properties, allowing customization based on specific application requirements. Acrylic resin coatings that are crosslinked with amino compounds exhibit greater resistance to chemicals, solvents, and environmental factors, which increases the lifespan of the coated surfaces [10,14–16]. Among the amino resins adopted as crosslinkers for acrylic resins are melamine [17–20], urea [21], benzoguanamine [22], and glycoluril [23].

The selection and optimization of crosslinking agents used in varnishes for beverage can coatings play a crucial role in determining the coatings' dimensional stability and overall performance. Studies, such as that of Jiao et al. [24], have shown that the mechanical properties of acrylic resins, such as tensile strength, impact strength, and surface hardness, can be significantly influenced by the selection of appropriate crosslinking agents. In particular, a high degree of crosslinking tends to result in strong mechanical properties. Additives can also improve mechanical properties by enhancing the crosslinking effect, reducing pore volume, refining pore structure, and improving overall composite properties. Additionally, the ratio of hard and soft monomers can impact mechanical properties, emphasizing the importance of careful monomer selection. Another study by Licbarski et al. [25] highlighted the significance of a meticulous approach to selecting the appropriate crosslinking agents for improved performance.

An important drawback of crosslinking agents when stored for extended periods is their susceptibility to precipitation, which can be caused by reactions with impurities or degradation. This can lead to reduced solubility and the formation of solid particles in the solution, which affects the performance and adhesion properties of the coating material. To prevent reduced solubility and adhesion issues in coating materials, it is crucial to store amine crosslinking agents correctly. Airtight containers, controlled temperatures, and quality control measures help to ensure their purity and stability. Following recommended handling procedures, avoiding contamination, and using stabilizers or inhibitors to enhance long-term stability are important measures. Implementing a first-in, first-out inventory management system also reduces prolonged storage.

A comprehensive explanation of recent developments in beverage metal can coating technology, particularly in the context of US' regulatory considerations, the industry's response to increasing regulatory pressure, and the need for innovative can coatings, can be found in [26,27]. The former covers the technology of can fabrication, the processing of can contents, and US regulations regarding can coatings. It also highlights recent research on can coatings and provides insights into the evolving landscape of can coating technology in the US. Dubail [27] details the obstacles the industry faces as it strives to create new technologies free from BPA, a component commonly found in traditional epoxy coatings. The European Food Safety Authority (EFSA) recently published a new scientific opinion that significantly reduced the tolerable daily intake (TDI) of BPA, prompting the industry to shift towards non-BPA alternatives for food contact materials throughout Europe. In response to these regulatory and consumer pressures, the industry has developed its first non-BPA epoxy coating technology, valPure® V70. This innovative technology provides comparable performance benefits to traditional epoxy coatings, allowing for the use of metal cans in challenging packaging scenarios. The development process involved the collaboration of third-party entities to ensure regulatory compliance and safety. The article also focuses on the growing markets for canned wine and water, which require specialized can coatings to facilitate the transition to metal packaging. It underscores the importance of developing high-performance technologies to meet evolving packaging requirements.

Within this context, this study aimed to explore different coatings for aluminum beverage cans to improve their physical resistance and prevent corrosion and surface damage. To this end, an acrylic resin was combined with six different amino resins (methylated melamine, butylated melamine, glycoluril, methylated urea, butylated urea, and benzoguanamine) in various ratios, and the outcomes were compared. A total of 25 samples were created and tested for their adhesion, durability, and chemical resistance properties.

2. Methodology

Standard industry methods were used to prepare exterior varnish samples while maintaining consistent guidelines. A standard water-based acrylic resin was produced, followed by varnish production with crosslinking agents.

2.1. Preparation of the Water-Based Acrylic Resin

The reagents used in synthesizing the acrylic resin, as well as their function and proportions, are shown in Table 1.

Acrylic resin production was performed according to the following procedure.

(1) Butyl glycol was added to a three-neck volumetric flask and heated to 135–140 °C;
(2) In another vessel, acrylic acid, styrene, methyl methacrylate, and butyl acrylate were mixed (premix 1) and stirred for 15 min, after which the acidity index (95–100) was determined; then, benzoyl peroxide was added, and stirring was maintained for another 15 min;
(3) To the volumetric flask, at a temperature of 135–140 °C, premix 1 was added dropwise, totaling 4 h of addition under constant stirring;
(4) In another vessel, dimethylethanolamine and water were mixed and stirred for 15 min (premix 2);
(5) After the complete addition of premix 1 into the flask, the temperature was lowered to 98–100 °C, and premix 2 was added, totaling 30 min of addition. Next, the flask was cooled, and after 24 h, quality control tests were performed.

Table 1. Acrylic resin formulation.

Item	Reagents	Function	%
1	Butyl glycol	diluent controlling system isothermy	8.000
2	Acrylic acid	monomer aiding in the formation of the carboxylic functional group	4.375
3	Styrene	monomer assisting in increasing the molecule size, contributing to shinier finish	10.736
4	Methyl methacrylate	monomer increasing the varnish hardness and Tg	8.947
5	Butyl acrylate	monomer aiding in flexibility	10.942
6	Benzoyl peroxide	reaction initiator	0.150
7	Dimethylethanolamine	neutralizes and aids in water solubility	2.706
8	Water	diluent solvent	54.144
		Total	100

2.2. Preparation of the Varnishes

As mentioned in the introduction section, amino crosslinkers improve the adhesion of acrylic resin coatings to different surfaces, making the coatings more durable and stronger. Hence, to prepare varnishes from the acrylic resin, six amino crosslinking agents were used: methylated melamine (MM), butylated melamine (BM), methylated urea (MU), butylated urea (BU), benzoguanamine (BG), and glycoluril (GL). The chemical structures of the agents are shown in Figure 1.

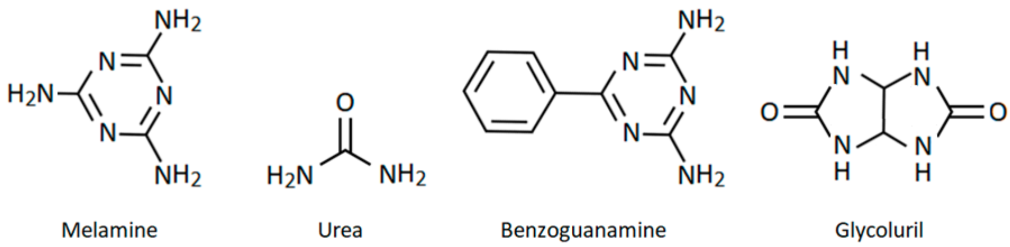

Figure 1. Chemical structures of crosslinking agents.

A Fisaton stirrer with a Cowles-type disperser was used for all preparations at a speed of 1000 rpm.

In the paints and varnishes industry, the standard formulation of a water-based acrylic varnish is based on a ratio of 70% resin to 30% crosslinking agent. This ratio is calculated based on the solids content of each component.

Twenty-five varnish samples were produced with resin/crosslinker ratios equal to or close to the industrial standard formulation to assess variations in performance. Varnish types 1, 2, and 3 had different proportions, with type 1 consisting of 80% resin to 20% crosslinker; type 2 was composed of 70% resin to 30% crosslinker; and type 3 comprised 60% resin to 40% crosslinker. For type 4, stoichiometry was calculated based on the functionality of each raw material tested. Figure 2 illustrates the nomenclature of the varnish samples with their resin-to-crosslinker ratio.

After preparation, various chemical and physical tests were carried out to determine the best results. The varnishes were cured in two stages: a pre-cure for 1 min at 205 °C and a final cure for 3 min at 205 °C.

Paint and coatings companies use various testing methods to assess the quality of their products; some are based on ABNT (Brazilian Association of Technical Standards) or ASTM (American Society for Testing and Materials) standards, and others are specific to the field of paint application.

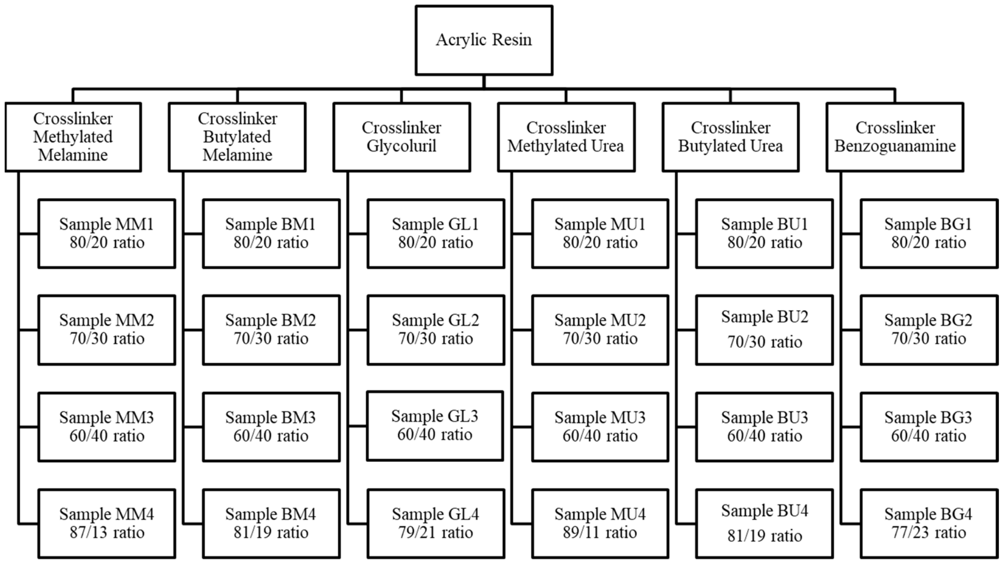

Figure 2. Varnish samples prepared at different acrylic resin-to-crosslinker ratios.

2.3. Testing of the Varnishes

A scoring system was used for each test to evaluate the quality of the varnish. The importance of each test was considered when assigning scores ranging from 1 to 3. Tests without specific approval targets, such as determining specific mass, viscosity, nonvolatile content, and pH, were given a score of 1. Tests with approval targets deemed most important in the industry for overall performance were given a score of 3, i.e., the mechanical tests, and those with approval targets but of lesser importance to overall performance scored 2.

All tests conducted are presented along with their scores. Tests that were performed following private technical standards rather than standard organizations or systems, such as ASTM or ISO, are outlined in the Supplementary Materials.

- Tests on Varnish in the Liquid State:
    - Determination of specific mass (ASTM D1475)—score 1;
    - Determination of viscosity by Ford Viscosity Cup (25 ± 1 °C) (ASTM D1200)—score 1;
    - Determination of nonvolatile content—2 h at 135 ± 3 °C (ASTM D2832)—score 1;
    - pH determination (ASTM D4584)—score 1;
    - Appearance of the liquid varnish (Private Technical Standard used in paint and varnish industries)—score 2;
    - Accelerated stability of the liquid varnish (ASTM D869)—score 2.
- Tests with Varnish Applied on A4 Aluminum Sheets (0.213 mm thickness) Supplied by the Beverage Can Manufacturer (identical to production line material):
    - Appearance of the applied film (Private Technical Standard used in paint and varnish industries)—score 2;
    - Appearance of the applied film after accelerated stability testing (Private Technical Standard used in paint and varnish industries)—score 2;
    - Tack determination: to assess drying level (Private Technical Standard used in paint and varnish industries)—score 2;
    - Adhesion determination (between two films or between a film and the substrate) (ASTM D3359)—score 2;
    - OMICRON—WEDGE BEND Impact Test: evaluates flexibility of enamels and varnishes used as coatings on metal packaging (ASTM D2794)—score 3;
    - Hardness measured with a Clemens manual sclerometer (wedge-tipped probe) (ASTM D2197)—score 3;

- Resistance to scratches using the SHEEN TEST method (ISO 1518)—score 2;
- Mobility Test—ALTEK: determines the coefficient of friction of coated surfaces (Private Technical Standard used in paint and varnish industries)—score 3;
- MEK Resistance Test: determines chemical resistance of the varnish (ASTM D5402)—score 2;
- Methyl Violet Resistance: determines varnish/paint curing degree via methyl violet absorption (Private Technical Standard used in paint and varnish industries)—score 2;
- Pasteurization with beer, pasteurization with detergent, and pasteurization with water: detergent test simulates can washing at the end of the filling process (Private Technical Standard used in paint and varnish industries)—score 2.

When adding up the values, a varnish's maximum score is 41 points, i.e., the varnish meets all the market requirements for cans.

The most promising materials were subjected to thermal treatments, where FTIR (Fourier-transform infrared) analyses were conducted before and after curing. After curing, the samples were vacuum-dried for 15 h to remove the solvent. Subsequently, they were exposed to curing temperatures to assess the changes that occurred before and after curing. Samples were subjected to Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy in the region between 4000 and 400 cm^{-1}, with a resolution of 4 cm^{-1} and 128 scans, in a Thermo Fischer Scientific FTIR spectrometer.

3. Results and Discussion

The Supplementary Material features graphs displaying the outcomes of all of our tests. In the following, a discussion of the test results ensues. Scores were assigned to those samples that met the targets established for each test, while samples that did not meet the necessary criteria did not receive a score.

3.1. Determination of Specific Mass, Viscosity, Nonvolatile Content, and pH

For the paint and varnish industry, these tests are essential for controlling batches of products, but in the case of development, there is no established approval target.

All specific mass results were close, ranging between 1.02 and 1.06 g/cm^3. The Ford cup viscosity ranged from 41 to 63 s. To meet the unique requirements of each piece of equipment in the customers' production lines, viscosity is fine-tuned accordingly.

The findings regarding the non-volatile content of the varnishes were consistent, with results ranging from 35 to 36%. Typically, varnishes with a higher solids content lead to a greater yield. Consequently, can companies benefit from varnishes with higher solids content as they facilitate increased can production.

The pH values fell within a narrow range of 7.35 to 7.73. In the realm of beverage can manufacturing, it is advisable to maintain the pH level of the external coating between 6.5 and 8.5. This helps ensure better compatibility with the can label's printing ink.

3.2. Appearance of the Liquid Varnish

The possible results of this test are good, slightly separated, or separated. And the desired target is good.

On the first day of production, all samples had a similar appearance and met the necessary criteria. Hence, all samples received a score of two. However, it is common for varnishes to require more time for particle settling, resulting in positive results.

By day 10, only the MM3, GL3, BG2, and BG3 samples met the satisfactory standards. Therefore, in the 10-day test, only these samples received a score of two. The remaining samples were ranked as being unsatisfactory because the particles settled over the 10 days, allowing for the level of separation to be observed. Although it is desirable for varnish to not exhibit any separation, approximately 90% of commercial varnishes do have this characteristic.

While varnish with separation may not have performance problems, it can cause visual issues and increase expenses for agitators as storage tanks will require 24 h agitation, resulting in additional costs. One possible cause of phase separation is using raw materials with different specific densities, such as particulate waxes. Although waxes are needed to achieve a good amount of slip, not all are fully compatible with the medium.

After 30 days of production without agitation, all of the samples became unsatisfactory, showing particle sedimentation. Hence, the samples received no scoring, as can be seen in Table 2.

3.3. Appearance of the Applied Film after Accelerated Stability Testing (16 h at 60 ± 5 °C)

Like the previous test, the outcome of this test can be categorized as good, slightly separated, or separated. The desired target is good. The process of accelerated stability testing emulates the natural aging of varnish. Therefore, if all varnishes failed to meet the appearance criteria in the 30-day test, it is reasonable to expect that they would also perform poorly in the accelerated stability test. Out of all the samples tested, only BG3 yielded satisfactory results. Nevertheless, the outcome falls short of the necessary approval standards.

3.4. Appearance of the Applied Film

The possible outcomes of this test are good, slightly cloudy, or cloudy, with the desired target being good.

The AR sample failed to form a film because it lacked a crosslinking agent to finalize the reaction. As a result, this sample remained noticeably sticky and did not dry. The following samples proved to be successful: MM1, MM2, MM3, MM4, MU1, MU2, MU3, MU4, BG1, BG2, BG3, and BG4. However, the GL and BU samples exhibited slight cloudiness, while the BM samples became cloudy. Hence, the MM, MU, and BG samples received a score of two.

3.5. Appearance of the Applied Film after Accelerated Stability Testing

Film appearance can yield several results, including good, slightly cloudy with craters, slightly cloudy with orange peel, and orange peel with craters. The desired target is good. Samples that showcased a satisfactory appearance after 16 h at 60 ± 5 °C include MM1, MM2, MM3, MM4, BG1, BG2, BG3, and BG4.

3.6. Tack Determination: To Assess the Drying Level

The results yielded in this test are good or tacky. The desired outcome is good, and the following samples demonstrated satisfactory results: MM1, MM2, MM3, MM4, BM2, BM3, GL1, GL2, GL3, GL4, MU1, MU2, MU3, MU4, BG1, BG2, BG3, and BG4. These samples were thoroughly dry and received a score of two.

3.7. Adhesion Determination

During the adhesion test, none of the samples had any film detachment from the test specimens. This indicates that the adhesion quality was not affected by the different types of crosslinking agents and variations in concentration. Consequently, all samples received a score of two.

3.8. Omicron—Wedge Bend Impact Test

The target of this test is 0% detachment of the varnish at the fold area of the coated aluminum sheet folded in a U-shape when subjected to impact. This means that the varnish has sufficient flexibility. Flexibility is essential for forming cans because the varnish, after application, goes through approximately 25 presses for the complete formation of the can. The lower the % of detachment, the better the result. Only samples MM3, GL1, GL2, GL3, and GL4 showed 0% detachment, so they received a score of three.

Table 2. Results of practical tests, scored for performance.

		Samples with Their Attributed Scores																								
Scores	**Tests**	**AR**	**MM1**	**MM2**	**MM3**	**MM4**	**BM1**	**BM2**	**BM3**	**BM4**	**GL1**	**GL2**	**GL3**	**GL4**	**MU1**	**MU2**	**MU3**	**MU4**	**BU1**	**BU2**	**BU3**	**BU4**	**BG1**	**BG2**	**BG3**	**BG4**
1	Specific gravity	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	Viscosity	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	Non-volatile content	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	pH	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	Appearance of liquid varnish day 1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
2	Appearance of liquid varnish day 10				2								2											2	2	
2	Appearance of liquid varnish day 30																									
2	Appearance of liquid varnish after accelerated stability																									
2	Appearance of film		2	2	2	2									2	2	2	2					2	2	2	2
2	Appearance after accelerated stability		2	2	2	2																	2	2	2	2
2	Tackiness		2	2	2	2		2	2		2	2	2	2					2	2	2	2	2	2	2	2
2	Adhesion		2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
2	Sheen test			2	2		2	2	2		2	2	2		2	2	2						2	2	2	
2	Resistance to MEK			2	2							2	2												2	
2	Resistance to methyl violet				2																				2	
2	Pasteurization with beer		2	2	2	2					2	2	2	2									2	2	2	2
2	Pasteurization with detergent		2	2	2	2					2	2	2	2									2	2	2	2
2	Pasteurization with water		2	2	2	2					2	2	2	2					2	2	2	2	2	2	2	2
3	Wedge bend				3						3	3	3	3												
3	Clemens sclerometer hardness			3	3							3	3										3	3	3	
3	ALTEK mobility test			3	3																			3	3	3
41	total score	6	20	30	37	20	10	12	12	8	21	26	28	19	12	12	12	10	12	12	12	12	25	30	34	23

3.9. Hardness Measured with a Clemens Manual Sclerometer

A wedge-shaped tip rod is used in tandem with weights of increasing mass until the varnish begins to be removed. The minimum target is 400 g, with the results expressed comparatively and measured in grams. This test simulates the abrasion that can occur between cans during filling and transportation to the end consumer. In the study, samples MM2, MM3, GL2, GL3, BG1, BG2, and BG3 demonstrated satisfactory outcomes, yielding 400 g or more, and, therefore, they received a score of three. It should be noted that samples BG2 and BG3 surpassed the performance of the specimens above, registering 450 g. This distinction underscores the superiority of BG2 and BG3 compared to their counterparts within the experimental framework.

3.10. Resistance to Scratches Using the SHEEN TEST Method

The scratch resistance of the film is evaluated through the penetration of a spherical tip. The automatic device ceases operation at the onset of film rupture, with the ideal weight target set at 700 g. Samples MM2, MM3, BM1, BM2, BM3, GL1, GL2, GL3, MU1, MU2, MU3, G1, G2, G3 showed satisfactory results, with MM3 and GL2 presenting a superior result of 800 g, while GL3 achieved 900 g. Generally, the varnish is more resistant to scratches when higher weights are required for film rupture onset.

3.11. Mobility Test—ALTEK

In this test, as described in the Supplementary Material, the target for an approved varnish is a coefficient of friction value of up to 0.070. The results for samples MM2, MM3, BG2, BG3, and BG4 all met the specified criteria. It is worth noting that a lower Altek value correlates with a more favorable outcome in this instance.

3.12. MEK Resistance Test

The chemical resistance of the varnish is determined by its MEK resistance. Friction tests are conducted by swabbing a cotton swab moistened with MEK in the same area, both forward and backward. A desirable outcome is a value of over 100 frictions without removing the varnish layer. For accuracy's sake, a standard is used for comparison. Samples MM2, MM3, GL2, GL3, and BG3 demonstrated satisfactory results, achieving 100 frictions, while the remaining samples yielded between 10 and 60 frictions.

3.13. Methyl Violet Resistance

The degree of varnish curing is determined through the methyl violet resistance test by measuring its absorption. The ideal outcome is achieved when there is zero absorption of methyl violet, indicating full curing of the varnish. Out of the samples tested, only MM3 and BG3 exhibited satisfactory results.

3.14. Pasteurization with Beer, Detergent, and Water

The appearance and adhesion properties of the MM, GL, and BG varnish samples exhibited stability post-pasteurization across the three test mediums. Furthermore, the integrity of the BU varnish samples was preserved exclusively in instances where water was employed as the pasteurizing agent. Therefore, MM1 to MM4, GL1 to GL4, and BG1 to BG4 received a score of two for the three tests, whereas BU1 to BU4 received this score only for the test with water, as can be seen in Table 2

Table 2 presents the scores obtained for all varnish samples that underwent the tests mentioned in the previous section. The varnish containing the methylated melamine crosslinker at a ratio of 60% resin to 40% crosslinking agent (MM3) displayed the best performance, scoring a total of 37 out of 41. The second-best performance was observed for the varnish containing the benzoguanamine crosslinker at a 60/40 ratio, with a score of 34.

3.15. FTIR

Figures 3–6 show the FTIR-ATR spectra of the samples with the best performance (MM3 and BG3) as well as those with the poorest performance, i.e., the acrylic resin without a crosslinker (AR) and the BM4 sample, before and after curing.

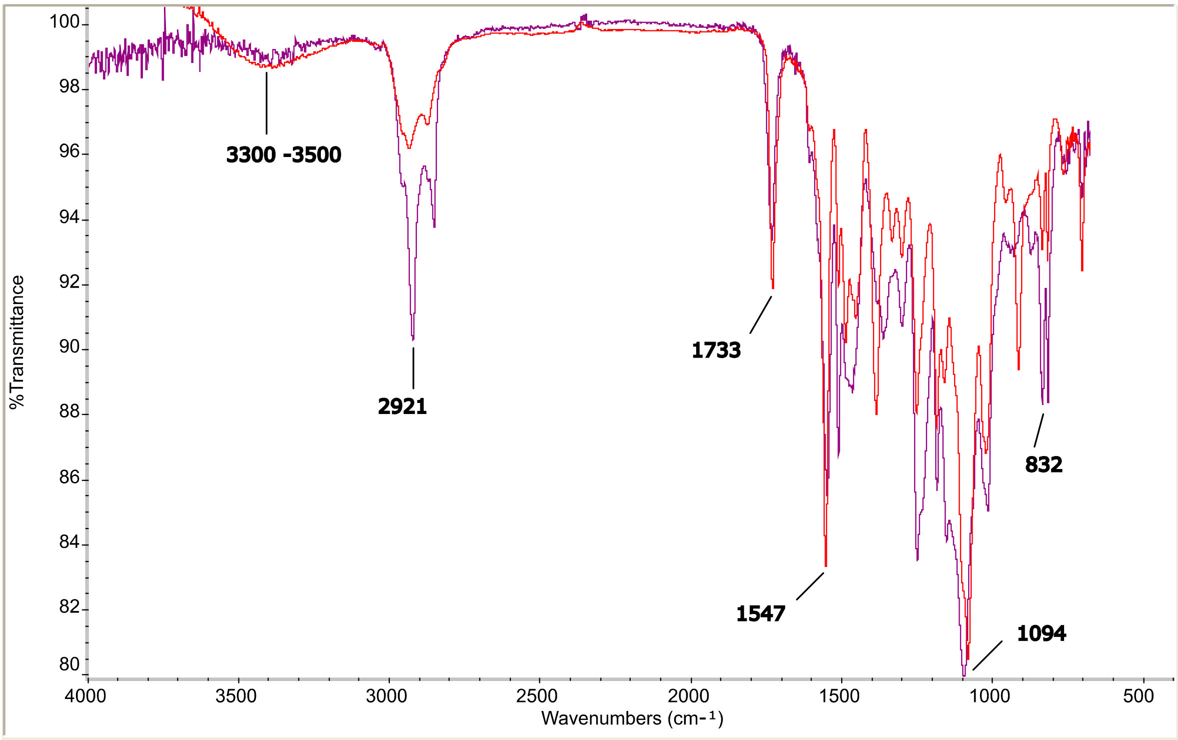

Figure 3. FTIR spectra of the MM3 sample before curing (red) and after curing (violet).

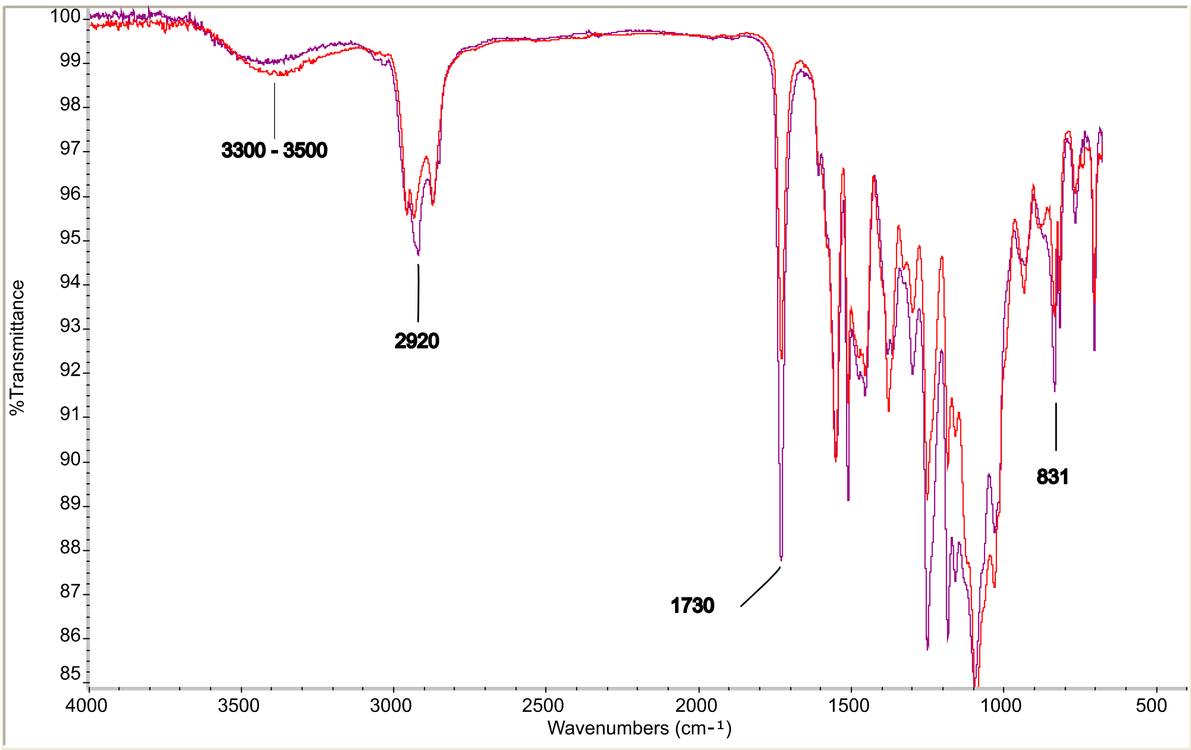

Figure 4. FTIR spectra of the BM3 sample before curing (red) and after curing (violet).

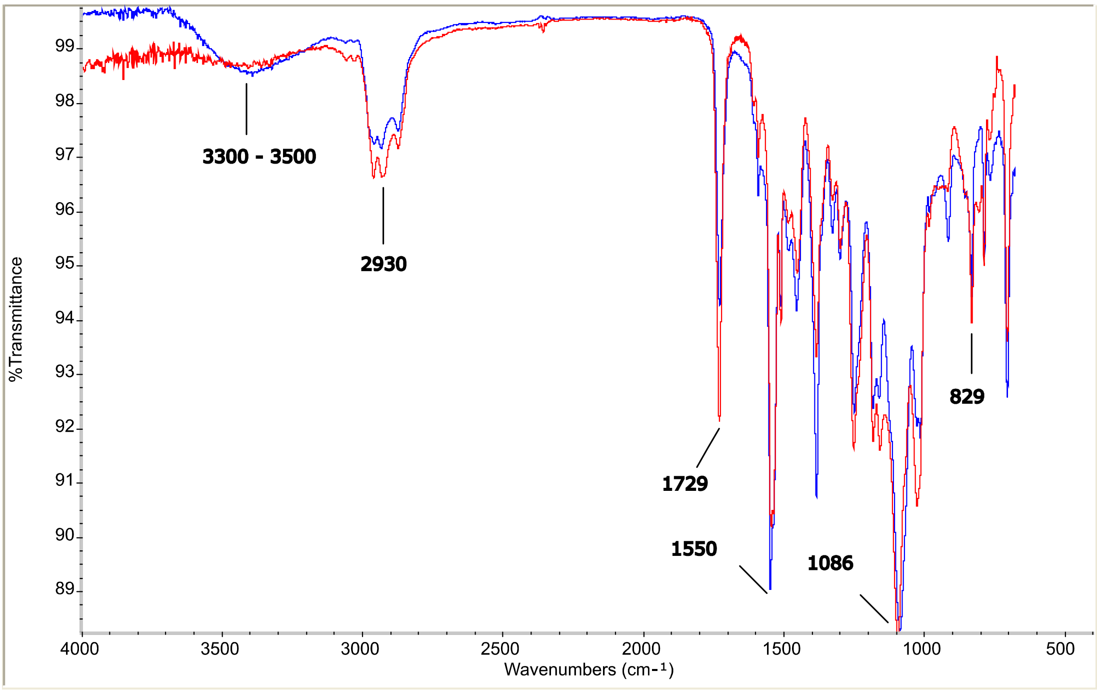

Figure 5. FTIR spectra of the BG3 sample before curing (blue) and after curing (red).

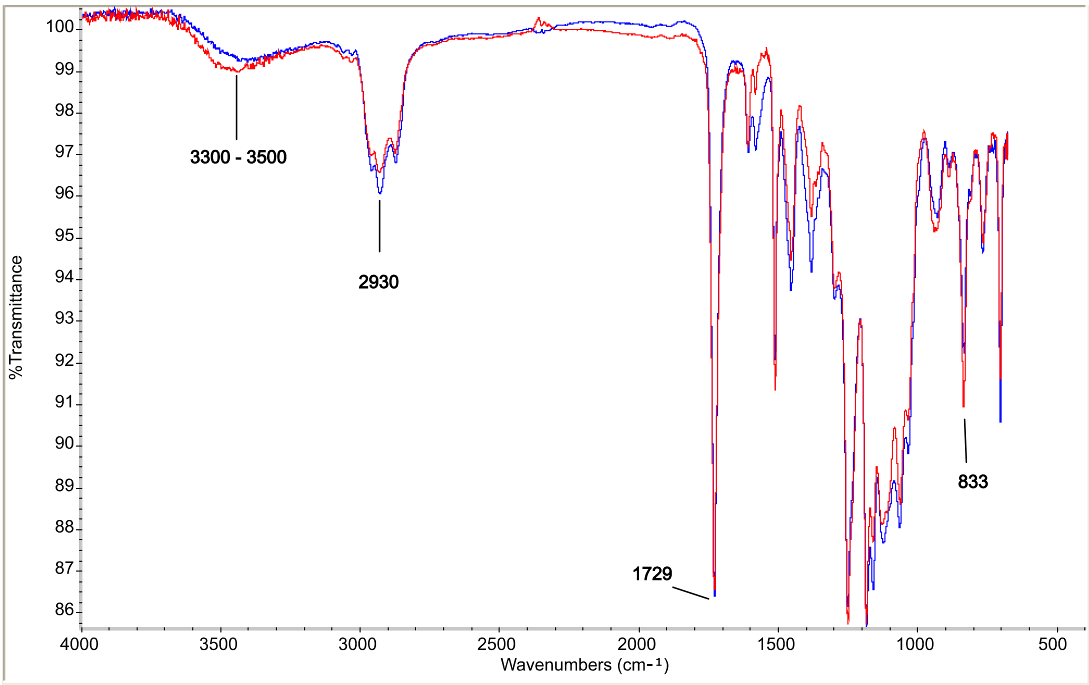

Figure 6. FTIR spectra of the AR resin sample without crosslinker before curing (blue) and after curing (red).

The observations of changes in the FTIR spectra peaks after curing are highly relevant for understanding the chemical reactions during the process. Several conclusions can be drawn from these observations.

Figure 3 displays the FTIR-ATR spectra for the varnish with the best performance, which used methylated melamine crosslinker at a ratio of 60% resin to 40% crosslinking agent.

Figure 4 presents the FTIR results for the varnish that exhibited the second-best performance, which utilized the crosslinking agent benzoguanamine at a ratio of 60% resin to 40% crosslinking agent.

Conversely, the varnishes with the crosslinking agent butylated melamine, at a ratio of 81% resin to 19% crosslinking agent, demonstrated the poorest results; the spectra of which are shown in Figure 5. Furthermore, the spectra of the varnish formulation without a crosslinking agent, which also displayed poor performance, are shown in Figure 6.

The following changes in absorption bands have been observed.

Increase in the 2920 cm^{-1} band: The intensification of the band at 2920 cm^{-1}, associated with the methylol group, suggests the occurrence of crosslinking reactions. This increase indicates a higher formation of crosslinks between polymer chains, which is desirable to improve the properties of the varnish.

Decrease in the 3500–3300 cm^{-1} band: The reduction in the OH^- band in this wavelength range is related to the extent of curing. The less intense this band, the greater the likelihood that the sample is fully cured. This means that the crosslinking reaction was effective, reducing the presence of OH^- groups [12].

The peaks around 1700 cm^{-1} correspond to carboxylic acid groups from the acrylic resin. The presence of these groups is essential, but an excess of them can increase the solubility of the varnish in water.

The peak at 831 cm^{-1} is attributed to the triazine group originating from the melamine resin. This suggests that the crosslinking reaction effectively occurred between melamine and acrylic resin, contributing to the formation of crosslinks in the polymer matrix.

Table 3 shows the assignments of the important peaks discussed so far.

Table 3. Assignments of the important FTIR peaks.

Wavenumber (cm^{-1})	**Vibration**	**Function**
3500–3300	O-H stretch	Hydroxyl
2961	CH_3 stretch	Alkane
2920	CH_2 stretch	Alkane
1732	C=O stretch	Carbonyl
1550	N-H stretch	Amine
1093	C-O stretch	Ether
831	angular deformation of the ring	Triazine

These interpretations of the FTIR results provide valuable insights into the chemical transformations that occur during the curing of varnishes, aiding our understanding of the performance of different formulation systems and the identification of the best options for specific applications.

4. Conclusions

The study examined the effects of different crosslinking agents on varnish performance and found that they significantly improved the varnish's chemical and physical resistances. Each crosslinking agent demonstrated unique properties, and the best ones for the tested composition were the samples containing methylated melamine and benzoguanamine, as determined by the criteria established in this study.

Increasing the proportion of crosslinking agents in the mixture improved the varnish quality, especially when there was an excess in the stoichiometric ratio, calculated based on functionalities, at approximately 60% resin and 40% crosslinking agent. The FTIR analysis showed that the samples with the best results exhibited a decrease in the OH^- bands, indicating better curing. In contrast, the samples with poorer results did not exhibit significant peak changes before or after curing in the FTIR analysis.

This study highlights the significant impact of different crosslinking agents on varnish performance, emphasizing that their choice should be carefully considered based on the desired properties of the final product. The proportion of the crosslinking agent plays a crucial role in determining varnish quality, and increasing the proportion of the crosslinking agent, especially above the stoichiometric ratio, can improve varnish quality, including enhanced chemical and physical resistance.

The study has practical implications for the beverage can industry. It addresses the challenges related to the transportation and protection of aluminum cans, emphasizing the importance of varnish formulations to enhance resistance and durability. These improved properties have several impacts on manufacturers and consumers. Enhanced durability reduces production costs and waste and provides consumers with a better experience. Extended shelf life and improved aesthetics benefit both manufacturers and consumers. Improved recyclability aligns with consumer preferences for sustainable packaging. However, there are potential drawbacks. Advanced coatings may come at a higher cost; not all coatings may be compatible with the beverage or can material. Regulatory compliance is necessary, and transparency about safety and benefits is essential to address consumer concerns. Therefore, while advanced coatings offer numerous benefits, a balanced assessment of their opportunities and challenges is crucial for decision-making.

While this study identified promising crosslinking agents, there may be room for further optimization. Future research could explore a broader range of formulations and crosslinking agents to fine-tune the varnish properties for specific applications. Other potential areas include long-term performance evaluations to assess the durability of coatings under diverse environmental conditions, assessing the environmental impact of the coatings throughout their entire lifecycle, and exploring the creation of sustainable alternatives, such as utilizing bio-based polymers or eco-friendly additives.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings14050585/s1.

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References

1. Lestido-Cardama, A.; Sendón, R.; Bustos, J.; Nieto, M.T.; Paseiro-Losada, P.; Rodríguez-Bernaldo de Quirós, A. Food and beverage can coatings: A review on chemical analysis, migration, and risk assessment. *Compr. Rev. Food Sci. Food Saf.* **2022**, *21*, 3558–3611. [CrossRef]
2. Stevens, M.P. *Polymer Chemistry: An Introduction*, 3rd ed.; Oxford University Press: New York, NY, USA, 1999.
3. Slone, R.V. Acrylic Ester Polymers. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley Online Library: Hoboken, NJ, USA, 2003. [CrossRef]
4. Richey, B.; Burch, M. Applications for Decorative and Protective Coatings. In *Polymer Dispersions and Their Industrial Applications*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2002; pp. 129–132. [CrossRef]
5. Cunningham, M.F.; Campbell, J.D.; Fu, Z.; Bohling, J.; Leroux, J.G.; Mabee, W.; Robert, T. Future green chemistry and sustainability needs in polymeric coatings. *Green Chem.* **2019**, *21*, 4919–4926. [CrossRef]
6. Young, R.J.; Lovell, P.A. *Introduction to Polymers*, 3rd ed.; CRC Press Taylor & Francis G.: Boca Raton, FL, USA, 2011.
7. Tylak, G.Y. Thermosetting Acrylic Resins—A Literature Review. *Prog. Org. Coat.* **1985**, *13*, 333–345. [CrossRef]
8. Juffermans, J.P.H. The Chemistry and Physics of Low-Emission Coatings. Part 1. High-Solids Topcoats. *Prog. Org. Coat.* **1989**, *17*, 15–26. [CrossRef]

9. Rezaei, M.; Yari, H.; Amrollahi, S.; Mohseni, M.; Mirzazadeh, H. Chemo-mechanical modification of an acrylic melamine coating by the aid of Recent developments in crosslinking technology for coating resins a functional hyperbranched toughener to enhance its biological resistance. *Prog. Org. Coat.* **2019**, *136*, 105194. [CrossRef]
10. Hare, C.H. *Protective Coatings. Fundamentals of Chemistry and Composition*; Technology Publishing Company: Pittsburgh, PA, USA, 1994.
11. Solomon, D.H. *The Chemistry of Organic Film Formers*; John Wiley & Sons Inc.: New York, NY, USA, 1977.
12. Córdoba, C.A.; Collins, S.E.; Passeggi, M.C., Jr.; Vaillard, S.E.; Gugliotta, L.M.; Minari, R.J. Crosslinkable acrylic-melamine latex produced by miniemulsion polymerization. *Prog. Org. Coat.* **2018**, *118*, 82–90. [CrossRef]
13. Oldring, P.K.T.; Hayward, G. *A Manual for Resins Surface Coatings*, 2nd ed.; SITA Technology: London, UK, 1987.
14. Lambourne, R. Paint composition and applications—A general introduction. In *Paint and Surface Coatings: Theory and Practice*, 2nd ed.; Lambourne, R., Strivens, T.A., Eds.; Woodhead: Glossop, UK, 1999; pp. 1–18. [CrossRef]
15. PCI. Crosslinking with Amino-Functional Siloxane Resin Improves Flexibility of Bis-Phenol A Epoxy Paints. *Paints & Coatings Industry Magazine*. 2005. Available online: https://www.pcimag.com/articles/82902-crosslinking-with-amino-functional-siloxane-resin-improves-flexibility-of-bis-phenol-a-epoxy-paints (accessed on 17 April 2024).
16. Li, Z.; Lv, X.; Che, Z.; Liao, H.; Zheng, J. Performance test and pyrolysis kinetics of water-based acrylic acid-amino resin. *Prog. Org. Coat.* **2022**, *172*, 107101. [CrossRef]
17. Jones, F.N.; Chu, G.; Samaraweera, U. Recent studies of self-condensation and co-condensation of melamine-formaldehyde resins; cure at low temperatures. *Prog. Org. Coat.* **1994**, *24*, 189–208. [CrossRef]
18. Vargha, V.; Körmendy, Z. Time–Temperature–Transformation Analysis of an Acrylic-Amino Resin System. *J. Therm. Anal. Calorim.* **2005**, *79*, 195–203. [CrossRef]
19. Merline, D.J.; Vukusic, S.; Abdala, A.A. Melamine formaldehyde: Curing studies and reaction mechanism. *Polym. J.* **2013**, *45*, 413–419. [CrossRef]
20. Mistry, J.K.; Natu, A.M.; Van De Mark, M.R. Synthesis and Application of Acrylic Colloidal Unimolecular Polymers as a Melamine Thermoset System. *J. Appl. Polym. Sci.* **2014**, *131*. [CrossRef]
21. Santer, J.O. Etherified Amino Resins: Synthesis and Reactions in Surface Coatings Applications. *Prog. Org. Coat.* **1984**, *12*, 309–320. [CrossRef]
22. Li, W.; Xu, J.; He, X.; Zhang, J.; Zong, E.; Liu, X.; Fu, S. Preparation and characteristics of Aziridine-Benzoguanamine-Urea-Melamine-Formaldehyde resins. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *207*, 012015. [CrossRef]
23. Ooka, M.; Ozawa, H. Recent developments in crosslinking technology for coating resins. *Prog. Org. Coat.* **1994**, *23*, 325–338. [CrossRef]
24. Jiao, C.; Sun, L.; Shao, Q.; Song, J.; Hu, Q.; Naik, N.; Guo, Z. Advances in Waterborne Acrylic Resins: Synthesis Principle, Modification Strategies, and Their Applications. *ACS Omega* **2021**, *6*, 2443–2449. [CrossRef]
25. Licbarski, A.; Bartkowiak, M.; Czech, Z. Influence of Selected Crosslinking Agents and Selected Unsaturated Copolymerizable Photoinitiators Referring to the Shrinkage Resistance of Solvent-Based Acrylic Pressure-Sensitive Adhesives. *Polymers* **2022**, *14*, 5190. [CrossRef]
26. Bailey, A. US regulatory considerations and recent developments on can coatings. In *Global Legislation for Food Contact Materials*, 2nd ed.; Baughan, J.S., Ed.; Woodhead: Glossop, UK, 2022; pp. 145–169. [CrossRef]
27. Dubail, S. Can Coatings: Unlocking the Future of Sustainable Packaging. *Paints & Coatings Industry Magazine*, 17 July 2023. Available online: https://www.pcimag.com/articles/111588-can-coatings-unlocking-the-future-of-sustainable-packaging (accessed on 17 April 2024).