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Design, Characterization and Application of Acrylic Copolymers Derived from Hydroxy Functional Bio-Derived Macromolecules

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Abstract

In the present study, bio-ester polyol with unsaturation in its backbone was synthesized by using monobasic fatty acid, dibasic acid, and polyol. We designed the bio-ester polyols with three different hydroxyl values: 190, 250, and 300 mg KOH/g along with three different synthesis methods. The reaction mechanism begins with the ring opening of maleic anhydride, followed by its condensation and esterification with trimethylolpropane. The second primary hydroxyl group in trimethylolpropane then undergoes further esterification with fatty acids from soybean oil. This process ultimately yields an unsaturated, hydroxyl-functionalized macromolecule. The molecular structure of the macromer was characterized by Fourier transform infrared spectroscopy. We have successfully developed acrylic copolymers using the nine different macromers (BM1a, BM2a, BM3a, BM1b, BM2b, BM3b, BM1c, BM2c, BM3c). The hydroxyl groups (OH) of acrylic polyols on addition reacting with Desmodur N3390 (NCO) with an NCO:OH ratio of 1:1 form polyurethane (PU) linkage. Prepared PU was coated on mild steel panels. The mechanical properties were evaluated by cross-cut adhesion test, abrasion resistance, scratch hardness, impact resistance, and dynamic mechanical analysis. The surface properties of the panels were analyzed after the quartz ultraviolet B exposure. The properties of all the acrylic copolymers were compared. It was found that the effectiveness of cross-linking interaction between NCO entities of polyisocyanates and the hydroxyl units of acrylic polyols was excellent in all the copolymer samples. Among the nine acrylic copolymer batches PABM1a, PABM2a and PABM3a once cured with aliphatic polyisocyanate exhibited exceptional functional characteristics. The environmental impact of the binders was limited to the manufacture and transportation of the binder in a life cycle assessment. A brief analysis of bioresources-derived resin compositions, properties, and applications is critically outlined herein, along with its kg CO_2-eq for evaluation of the environmental impact.

Categories: Environmental and Sustainable Engineering, Environmental Engineering and Sustainability, Polymer Science and Engineering
Keywords: renewable, acrylate, coatings, polyurethane, life cycle analysis

Introduction

Bio-ester polyols, derived from monobasic fatty acids, dibasic acids, and polyols, constitute a bio-based class partially sourced from vegetable oil. They are extensively utilized in various coatings such as polyurethane (PU), acrylic, alkyd, alkyd-acrylic, and polyester-based paints, catering to architectural, wood, automotive, and industrial applications [1]. These coatings offer numerous advantages including high gloss with exceptional retention and excellent solvent resistance. However, they exhibit drawbacks like poor hydrolytic stability, acidity, and alkali resistance [2].

Unsaturated bio-ester polyols play a significant role in enhancing the acrylate system. Over the past fifty years, modification of unsaturated bio-ester polyols with styrene and other vinyl monomers such as vinyl toluene and methyl methacrylate has been extensively explored [3,4]. Hydroxyl-functionalized acrylic resins, typically with molecular weights (MWs) ranging from 15000 to 50000, serve as crucial binders for high-performance coatings. While these coatings enhance aesthetics and gloss, safeguarding substrates from environmental factors like sunlight, weather, chemical exposure, and mechanical damage is imperative. The efficacy of protective coatings hinges on their quality, with critical factors including scratch resistance and adhesion characteristics [4,5].

Fatty acid-derived bio-ester polyols demonstrate shortcomings in hydrolytic stability, often necessitating the use of organic solvents to manage viscosities. This limitation stems from the extended hydrocarbon chains introduced by pendant fatty acids, affecting their resistance to hydrolysis. Conventionally, the viscosities are altered by the use of different co-acrylates in acrylic polyols. The acrylic polyols lead to toxicity as they are derived from non-renewable materials. The use of bio-ester polyols allows for the incorporation of bio-based materials and reduces health hazards. If the viscosity is manageable with the higher solid contents, the volatile organic content (VOC) can be reduced, which is the leading issue in the coating industries. Due to the harmful effects of volatiles on the environment and human health, nowadays,

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the policies of manufacturing industries are aiming toward sustainable coating alternatives with low VOC emissions [6]. The key factor that we have identified to design a low VOC and sustainable coating is to synthesize new bio-based raw materials, which can help us to design polymers with lower viscosities and higher solid content. However, designing resins with the required properties is challenging due to conflicting characteristics such as fast drying and low viscosities; the lower glass transition temperature (Tg) and MW of the polymer will impart lower viscosity, but the higher MW and Tg will reduce drying time. Another alternative to reduce the viscosity of low VOC acrylic systems is to reduce the percentage of hydroxyl (OH)-functional-bearing monomer. However, reducing OH functionality will reduce the cross-linking density of the coating, which will further result in inferior mechanical properties [7-9]. Thus, designing the bio-ester polyol can lead to newer avenues toward sustainability.

The common challenges in the synthesis of bio-ester acrylic polyol are the durability and performance of the coating, processing of bio-based materials and their scalability, availability of the bio-based materials, and consistency in the quality. To address the given challenges, we have chosen a commonly available bio-source material as soybean oil fatty acid (SOFA). SOFA, as renewable components, has widely been consumed by the coating industry; its availability, low cost, and easy processability make it accessible to various industries. It has some drawbacks as the curable coatings has inherent softness due to presence of long fatty chain, which tend to lower the Tg of the material. Hence, there is a need for modification of this type of resin to increase the cross-link density and further incorporate rigid structure into the polymers. Additionally, the monomer incorporation exhibits the increase in gloss value, lowering the yellowness, and improvement in adhesion. SOFA is a promising raw material because of its abundant renewable source of soybeans, biodegradability, versatility to tailor properties such as flexibility, adhesion, hardness, and cost-effectiveness compared to other bio-derived feed stocks. SOFA has the following composition: oleic acid (23%), linoleic acid (51%), α-linolenic (10%), palmitic acid (10%), and stearic acid (4%) and it is classified under the semi-drying category of oils [10]. Dzunuzovic et al. synthesized a ultraviolet (UV) curable hyperbranched urethane oligomers using SOFA [11]. The synthesis of this reactive diluent required a two-stage process, which consumed more time and energy. This challenge can be overcome with a single-stage, energy-efficient process.

Traditionally, acrylic polyols or bio-ester polyols can be combined with polyisocyanates to create PU systems. PUs commonly utilize aromatic di-isocyanates like methylene diphenyl diisocyanate and toluene diisocyanate, which produce harmful aromatic diamine byproducts on degradation [12,13]. Hence, cycloaliphatic and aliphatic isocyanates such as isophorone diisocyanate and hexamethylene diisocyanate are preferable for synthesizing these polymer analogues [14]. Additionally, their UV resistance makes them suitable for transparent coatings [15]. Another crucial point is the PU industry's heavy reliance on fossil-based materials, prompting growing interest in renewable starting materials like amino acids, furan derivatives, sorbitol, lignin, cellulose, vegetable oils, and their derivatives to address environmental and economic issues [16-18].

Although several methods are available for assessing product life and its impact on the environment among academic and industrial practitioners, life cycle assessment (LCA) is widely accepted as a method for environmental assessment. Even though LCA has been standardized in ISO 14040 / ISO 14044 [19], the European Committee for Standardization, 2009 and 2018, provides methodical options, such as for selecting the system parameters, defining the functional entity, determining background tasks or choosing environmental impact assessment methods (European Commission, 2018). Among these, the cradle to grave approach is employed by many leading industries to capture global warming in terms of carbon footprint (kilogram of CO_2 equivalent), which is termed as kg CO_2-eq. In order to develop the theoretical understanding of the impact of materials or coating systems on the environment, they can be compared and further optimized.

In order to build a sustainable bio-derived material, this paper focuses on bio-derived ester polyol and its usage in acrylic-PU systems. SOFA is incorporated with different processing routes to reduce the carbon footprint and synthesis different bio-ester macromolecules with hydroxyl functionality, which further can cross-link with polyisocyanates. Additionally, we provide an overview of the different synthesis processes, their impact on properties, and life cycle assessment interpretation. We have specified requirements for impact by fossil, biogenic and land transformation, and impact on global warming to lower the environmental impacts.

Materials And Methods

Materials

The following raw materials were utilized in the experiments: trimethylolpropane (TMP) supplied by Perstorp Chemical, India; soybean oil fatty acid (SOFA) provided by Cargill India; maleic anhydride (MAN) sourced from Thirumalai; dibutyltin oxide (DBTO); and ortho xylene obtained from M/s. Sigma Aldrich (India). Styrene monomer was acquired from Supreme Industries, India, while butyl acrylate (BA) was procured from BASF Chemicals, India. Tertiary butyl per benzoate (TBPB) was received from M/s. Arkema Peroxides, India, and employed as the initiator. The polyisocyanate cross-linker hexamethylene-diisocyanate trimer, marketed under the trade name Desmodur N3390, was provided by Covestro AG, Germany. All the aforementioned materials were utilized as they were received in the conducted experiments.

Experimentation

Macromolecule Synthesis

TMP, MAN, and the bioresource acid such as SOFA were taken in a molar stoichiometric ratio to design the macromolecule polyols with hydroxyl value (-OH value) 190, 250, and 300 mg KOH/g. Polymerization was carried out by condensation at 200°C with stirring under a nitrogen atmosphere for 3 hours. The reaction schematic is mentioned in Figure *1*. The experimental setup comprises a Dean-Stark apparatus for continuous removal of the by-product (water) of esterification. Macromolecules are designed with hydroxyl value 190, 250, and 300 mg KOH/g, which are further denoted as BM1, BM2, and BM3, respectively.

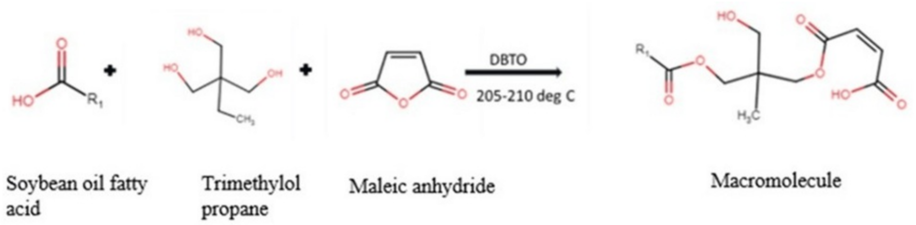

FIGURE 1: Reaction scheme for macromolecule based on bio-sourced fatty acid

DBTO, dibutyltin oxide

Different hydroxyl functional macromolecules were synthesized using three different routes: (a) MAN first reacted with TMP and then reacted with SOFA; (b) MAN, TMP, and SOFA reacted together; and (c) SOFA was esterified first with TMP and then added to MAN for its ring-opening (Figure *2*).

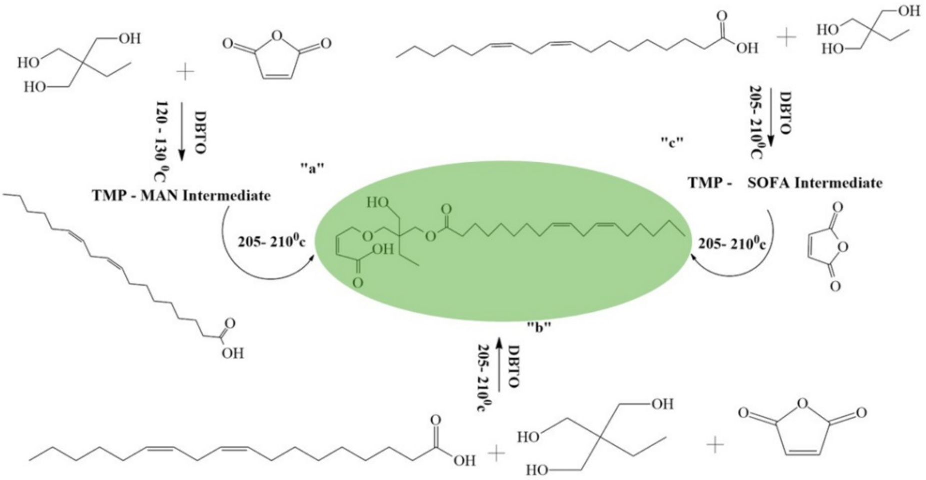

FIGURE 2: The schematic diagram for different approaches toward the synthesis of macromolecule

DBTO, dibutyltin oxide; MAN, maleic anhydride; TMP, trimethylolpropane; SOFA, soybean oil fatty acid

Co-acrylation of Macromolecule

Charge ortho-xylene into a 500-mL four-necked round-bottom flask armed with a stirrer, nitrogen channel, digital thermometer, and condenser. A predetermined quantity of styrene, BA, macromolecule, and TBPB was added through a peristaltic pump at a constant rate for 3 hours. During the charging of the monomer, the temperature was set up to 135°C, and a slow stream of nitrogen was started to avoid oxidation by atmospheric oxygen. After the addition of monomer, flushing of the peristaltic tube was done with ortho-xylene, and the temperature was raised to 142°C, and the batch was kept for digestion for the next 3 hours. Periodical monitoring of viscosity and % non-volatile content was done every 1 hour.

The polymers will be referred to as PABM1a, PABM2b, PABM3c. The a, b, c denote three different processes for synthesizing macromolecule, while BM1, BM2, BM3 representing three different hydroxyl values of the macromolecule with 190, 250, 300 mg KOH/g, respectively, as exhibited in Table *1*. PA (poly-acrylate) denotes copolymerization with styrene and BA having % non-volatile matter 70 and with hydroxyl value of 100 mg KOH/g. For example, in the nomenclature, “PA” stands for poly-acrylate, and “BM1a” stands for bio-based macromolecule with a hydroxyl value of 190, processed via “a” route.

Sr. No	Raw Materials Used	Quantity (% By Weight)	Quantity (% By Weight)	Quantity (% By Weight)
	Code	BM1	BM2	BM3
1	TMP	28.61	33.05	36.00
2	MAN	5.33	5.78	5.59
3	SOFA	59.74	57.76	55.00
4	o-Xylene	6.308	3.40	3.40
5	DBTO	0.012	0.01	0.01
6	Hydroxyl value (theoretical, mg KOH/g)	190	250	300

TABLE 1: Macromolecule synthesis

DBTO, dibutyltin oxide; MAN, maleic anhydride; TMP, trimethylolpropane; SOFA, soybean oil fatty acid

Film Preparation of Co-acrylate Macromolecule

The acrylic resins were cross-linked by Desmodur N3390 (NCO) with an NCO:OH ratio of 1:1. O-xylene was added to the hardener resin solution under manual mixing to bring the solids to a processable viscosity. Clear coats were prepared on mild steel 4 × 6 inch panels with 30-40 microns (dry film thickness). The films were allowed to dry and cure at ambient temperature (25°C and 50% relative humidity), and the coating properties were characterized after 48 hours and again after 7 days.

Materials characterization

The viscosity assessment of the resins was conducted using the Gardner scale at a temperature of 25°C. Chemical structure analysis of the acrylic copolymer was conducted via Fourier transform infrared spectroscopy (FTIR, frontier) spanning from 4000 cm^{-1} to 400 cm^{-1}. Thermal characterization was accomplished using the TA DSC 250 differential scanning calorimeter (DSC). Gel permeation chromatography (GPC) was employed to determine the MW distribution of acrylic copolymers. Mechanical properties of the cured acrylic copolymer film were examined using dynamic mechanical analysis (DMA), utilizing a TA Q800 DMA analyzer. Specimens were prepared with uniform dimensions (thickness: 5 mm, thickness variation: 2-2.95 mm). DMA was conducted under specific conditions: temperature ranging from −30 to 150°C at a rate of 3°C/minute, strain set at 0.1%, and frequency set at 1 Hz. Impact resistance testing was carried out following ASTM D2479 standards, while adhesion testing was done according to ASTM 3359 guidelines. Scratch hardness was evaluated according to the IS 101 standard. Abrasion resistance of the film was determined in compliance with ASTM D4060, utilizing a CS 10 wheel with a load of 0.5 kg per 600 cycles, and the weight loss was quantified in milligrams after the specified cycles.

Results

Results and discussion

Characteristic of Macromolecule

The TMP-MA-SOFA-based macromolecule was explored as an industrial reactive bio-based macromolecule, to replace high-cost hydroxyl functional acrylates. In this macromolecule study, different processes and OH value-based molecules are synthesized, and their physiochemical properties are evaluated, and results obtained are shown in Table *2*.

Parameter/Batch No.	BM1a	BM2a	BM3a	BM1b	BM2b	BM3b	BM1c	BM2c	BM3c
Gardner color scale	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4
Clarity and appearance	Clear viscous liquid	Clear viscous liquid	Clear viscous liquid	Clear viscous liquid	Clear viscous liquid	Clear viscous liquid	Clear viscous liquid	Clear viscous liquid	Clear viscous liquid
Gardner consistency at 25ºC on Gardner scale	J-	P-	P-Q	M-N	R-S	P-Q	K-L	O-P	P-Q
Acid value (mg KOH/g)	8.59	8.51	10.23	8.05	7.61	8.47	9.34	7.38	10.38
% NVM at 120ºC/60 minutes	90.31	90.15	90.68	92.45	91.13	90.18	90.25	90.25	90.85
Hydroxyl number (mg KOH/g)	200.16	269.05	317.7	206.86	266.68	303.8	224.74	271.27	320.9

TABLE 2: Physiochemical properties of the macromolecules

FTIR analysis played a crucial role in identifying specific functional groups throughout various reaction stages. In all FTIR spectra of macromolecules, consistent characteristic bands with varying intensities were observed. The broad band around 3400 cm^{-1} reflects the OH functional group vibration within the macromolecules. Peaks around 2955 cm^{-1} and 2855 cm^{-1} signify the symmetric and asymmetric vibrations of aliphatic C-H bonds, confirming the existence of the added fatty acid chain in the macromolecule. A strong signal at approximately 1730 cm^{-1} points to the vibration of the -COOC- group within the macromolecule.

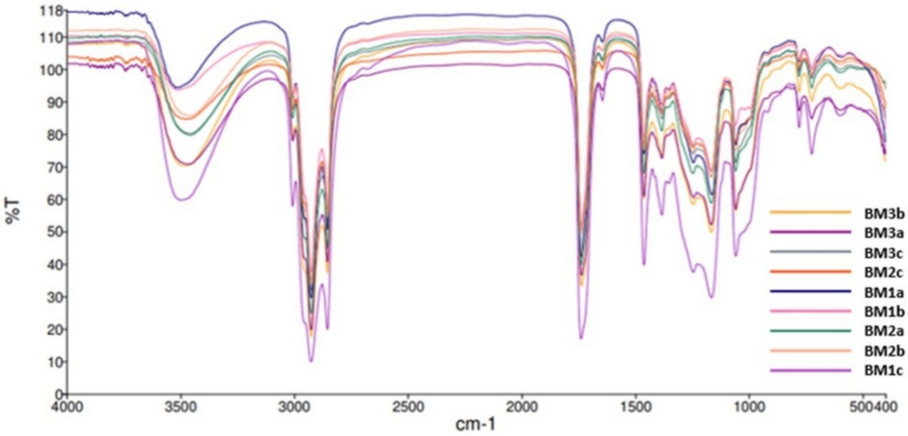

FIGURE 3: FTIR spectra of macromolecule synthesis with different hydroxyl value

FTIR, Fourier transform infrared spectroscopy

Characterization and Evaluation as Copolymer Molecule

In this study, the macromolecule was used in combination with other acrylate monomers to increase the reactivity of the resin and further reduce the viscosity of the acrylic copolymer system. This also helps to provide renewable and workable substitutes to petroleum-based material without any deterioration in film-forming properties. These macromolecules were not alone as polyols since they are expected to have poor mechanical and thermal properties. Table *3* and Table *4* showcase the co-acrylation of the macromolecule and its physiochemical properties.

Sr. No	Raw Materials Used	Quantity (% By Weight)								
		PABM1a	PABM2a	PABM3a	PABM1b	PABM2b	PABM3b	PABM1c	PABM2c	PABM3c
1	Ortho xylene	24.6	26.8	27.5	26.8	25.9	27.5	25.9	26.9	26.5
2	Macromolecule	41.4	31.5	25.5	40	30.3	25.5	41	31.9	25.5
3	Styrene	27.2	33.3	36.7	26.2	35.3	37.3	26.2	33.3	38.9
4	BA	5.5	6.9	8.5	5.5	7.1	8	5.4	6.8	7.8
5	TBPB	1.6	1.6	1.9	1.6	1.6	1.8	1.6	1.5	1.4
	% Renewable content	24.73	18.19	14.02	23.90	17.50	14.02	24.49	18.42	14.02

TABLE 3: Formulation of co-acrylation of macromolecules

BA, butyl acrylate; TBPB, tertiary butyl per benzoate

	Acrylic Copolymer								
Parameter/Batch No.	PABM1a	PABM2a	PABM3a	PABM1b	PABM2b	PABM3b	PABM1c	PABM2c	PABM3c
Color	0-1	0-1	0-1	1-2	0-1	0-1	1-2	1-2	1-2
Clarity	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Haze
Viscosity at 25ºC on G scale	X-	Z1	Z1-Z2	V-W	Z3-Z4	Z4+	V-W	Y-Z	Z1+
Acid value (mg KOH/g)	5.74	5.69	5.19	5.27	5.29	5.75	5.21	4.09	5.5
% NVM at 150ºC/30 minutes	70	68.72	68.69	68.54	69.78	68.88	68.86	68.12	68.82
Hydroxyl value (mg KOH/g)	100	100	100	100	100	100	100	100	100
Molecular weight by GPC									
Mn	1834	1984	1988	1743	2311	2186	1651	1939	2040
Mw	19743	19631	13742	16547	27252	42014	15791	14949	15704
Mz	74203	62907	36387	57183	99965	222534	53994	44028	41119
PDI	10.76	9.89	6.91	9.49	11.79	19.22	9.56	7.71	7.69

TABLE 4: Physiochemical properties of co-acrylated macromolecules

GPC, Gel Permeation Chromatography; PDI, Polydispersity Index

All samples displayed a higher Polydispersity Index (PDI). The "b" set of experiments showed higher weight average MW compared to other synthesis routes (a and c). These b set of copolymers, synthesized by dumping all raw materials at the initial stage, formed long-chain fractions with higher weight average MWs (PABM1b, PABM2b, and PABM3b had higher weight average MWs of 16547, 27252, 42014) because of these higher MW fractions, they are showing a very high PDI. The Z average MWs of these copolymer are showing a very high number of weight distribution, which is due to the formation of higher MW fractions in the system (PABM1b, PABM2b, and PABM3b had Z average MWs of 57183, 99965, and 222534, respectively).

Monitoring the Curing Process of Resin Mixtures by FTIR

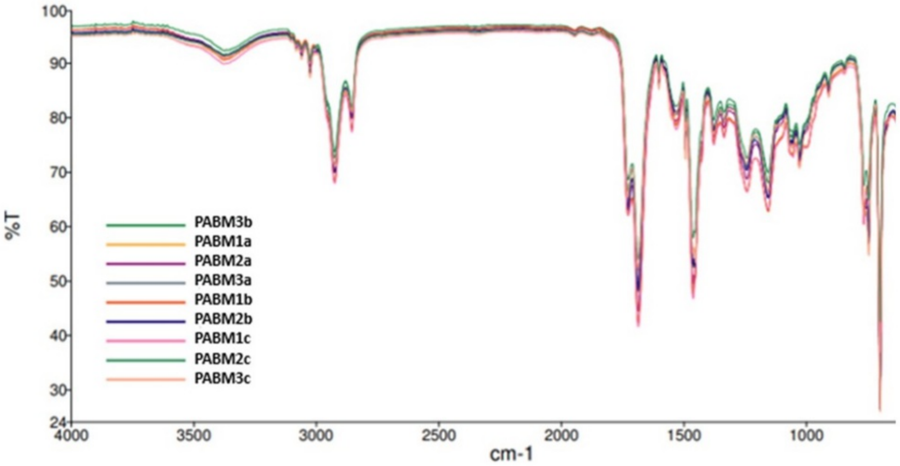

FIGURE 4: FTIR spectra of cured co-acrylate macromolecule

FTIR, Fourier transform infrared spectroscopy

Synthesized acrylate macromolecules were mixed with a polyisocyanate hardener at room temperature. FTIR spectra of the macromolecules are exhibited in Figure *3*, while cross-linked co-acrylate macromolecule spectra at room temperature are shown in Figure *4*. The FTIR spectra of different macromolecules exhibited changes in peak intensity for the cross-linked coatings, with notable peaks observed at approximately 3445 cm^{-1} (O-H stretch), 1732 cm^{-1} (C=O stretch), 1556 cm^{-1} (C-N stretch), 1386 cm^{-1} (C-H bend), 912 cm^{-1} (C-H bend), and 910 cm^{-1} (C-H bend). Additionally, a decrease in peak intensity was observed at approximately 3500 cm^{-1} (O-H stretch) for the cross-linked macromolecule coatings. A comparison between the FTIR spectra of the synthesized acrylate macromolecules and the cross-linked coatings reveals significant shifts and changes in peak intensities, indicating successful cross-linking and the formation of new chemical bonds.

Curing and film properties of co-acrylate macromolecules are discussed in Table *5* and comparison of cross-link density and Tg by DMA of cross-link co-acrylate macromolecule is exhibited in Table *6*.

Parameter/Batch No.	PABM1a	PABM2a	PABM3a	PABM1b	PABM2b	PABM3b	PABM1c	PABM2c	PABM3c
Surface dry time (minute)	40-45	40-45	40-45	40-45	20-25	40-45	45-50	40-45	40-45
Tack free time (hour)	5.5-6	4.5-5	4.5-5	5-5.5	6-6.5	4.5-5	5-5.5	4.5-5	4.5-5
Hard dry time in (hour)	8	8	8	8	8	8	8	8	8
Pot Life (hour)	>4	>4	>4	>4	>4	>4	>4	>4	>4
Cross-cut test for adhesion	5B	5B	5B	5B	5B	5B	5B	5B	5B
Abrasion resistance 0.5 kg load/600 cycles CS 10 wheel (mg)	25.1	12	20	45.5	28.2	34.1	26	20.8	30.5
Scratch hardness (g)									
After 48 hours	1500	1500	1400	1500	1500	1700	1300	1500	1400
After 7 days	2000	1800	1600	1500	1700	1900	1500	1500	1500
Impact, 7J	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Gloss at 60° (0 hours)	100.5	104.5	104	103.5	101	103.5	105	105	106
Gloss at 60° (after 500 hours of QUV B exposure)	102	101.5	Not tested*	100.5	99.7	97	103	102	100
Gloss at 60° (after 1000 hours of QUV B exposure)	92.7	83.5	Not tested*	74.5	75.7	80.5	91	96.5	88
Moisture content	0.09%	0.18%	0.10%	0.13%	0.15%	0.15%	0.15%	0.11%	0.13%

TABLE 5: Curing and film properties of co-acrylate macromolecules

*Not tested corrosion found in the panels after 300 hours of quartz ultraviolet B (QUV B) exposure.

Discussion

Mechanical and surface properties of the cured coatings

Results from the cross-cut adhesion test revealed that all synthesized macromolecule coatings exhibited exceptional adhesion to the mild steel panel, achieving the highest grade (5B). This strong adhesion may stem from interfacial adhesion mechanisms, such as compacted network polymer structures, which contribute to enhanced adhesion performance.

Hardness plays a crucial role in determining abrasion resistance across various coating applications. Abrasion resistance was assessed under a 0.5 kg load for 600 cycles with a CS 10 wheel. Systems "a" and "c" demonstrated superior abrasion resistance across all tested systems (BM1, BM2, BM3) exhibited in Figure *5*. This superiority could be attributed to the uniform MW distribution compared to process "b". Differences in polymer formation via the two-stage process and the dumping process might contribute to this variation. Additionally, the presence of polar urethane (-NH-COO-) groups in the tightly packed system further underscores the significance of interfacial adhesion.

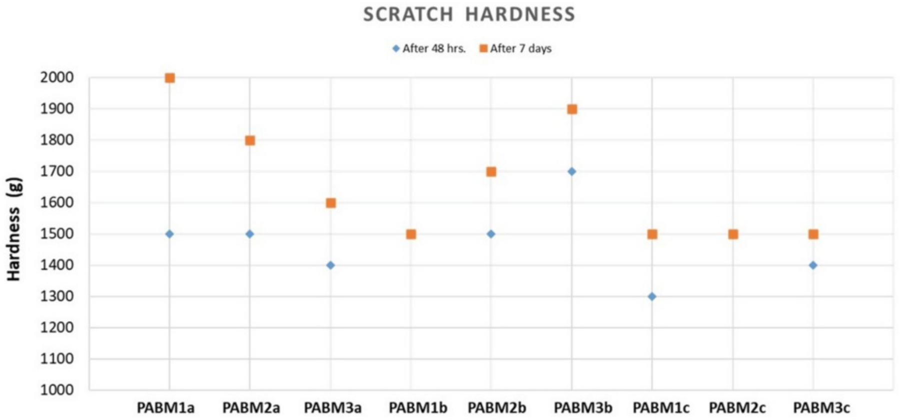

FIGURE 5: Comparison of hardness of cured film

The % gloss retention was determined after exposure to QUV B and found that 70% gloss was retained in all the samples. A lower PDI will help achieve better flow and film hardness and is also found to be excellent in % gloss retention. BM2c, BM1c, and BM1a based acrylic copolymer samples after 1000 hours of exposure show no film degradation with excellent % gloss retention. The varying polydispersity in the copolymer is due to the presence of monobasic acid in the macromolecule synthesis, which affects the PDI in radical formation. After 1000 hours of QUV B exposure, corrosion in the cured film was observed with the following trends: PABM3a > PABM2b > PABM3b > PABM3c > PABM1b > PABM1c > PABM1a = PABM2a = PABM2c exhibited in Figure 6. The higher acid value in the macromolecule tends to have a higher rate of corrosion, whereas in the "c" process, where MAN was added at the second stage, its copolymerization acrylate products, PABM3c and PABM1c, also show corrosion.

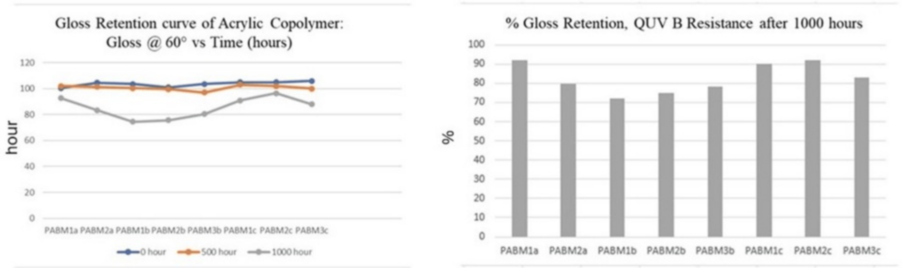

FIGURE 6: Gloss retention and % gloss retention after exposure of 1000 hours

QUVB, quartz ultraviolet B

DMA was performed using a TA Q800 analyzer, with specimens prepared to a standard width of 5 mm and thickness ranging from 2 to 2.95 mm. The analysis was conducted over a temperature range of -30 to 150°C, at a heating rate of 3°C/minute, with a strain of 0.1% and a frequency of 1 Hz. The study examined storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) as functions of temperature, with the Tg determined from the peak of the tan δ curve. Since the copolymers were synthesized by varying the macromolecule: styrene: BA ratio while maintaining a constant hydroxyl value of 100, the results provide insight into the impact of monomer composition on viscoelastic properties.

The storage modulus (E') varied considerably among the samples, reflecting differences in polymer rigidity. PABM2b (82.86 MPa) and PABM3c (157.3 MPa) exhibited the highest E' values, indicating increased stiffness, likely due to higher styrene content and greater cross-link density. In contrast, PABM1b (25.87 MPa) had the lowest E', suggesting a more flexible structure, likely influenced by a higher proportion of BA. This trend aligns with the Tg values, where PABM3c (44.3°C) and PABM2b (38.4°C) recorded the highest Tg values, whereas PABM1b had the lowest (30.1°C), confirming the effect of monomer composition on thermal transitions.

The tan δ values further support these observations. Higher tan δ values (1.011 for PABM1a) suggest increased molecular mobility and greater energy dissipation, characteristics of more flexible polymer networks. Conversely, lower values (0.7492 for PABM3b) indicate reduced damping behavior, associated with more rigid structures. The cross-link density (XLD) follows a similar trend, with higher XLD values (1.85×10^{-4} mol/cm³ for PABM1a) corresponding to increased stiffness and improved mechanical properties.

The cross-linking reaction efficiency between NCO entities of polyisocyanates plus hydroxyl functional groups of acrylic polyol was consistently excellent across all copolymer samples.

DMA Results	Film Thickness (mm)	E'25 (MPa) (Storage Modulus)	E"25 (MPa) (Viscous Modulus)	Tg (˚C)	Tan δ	XLD (mol cm^{-3})
PABM1a	2.23	40.34	34.51	32.6	1.011	1.85×10^{-4} at 66.12˚C
PABM1b	2.95	25.87	21.92	30.1	0.8978	1.53×10^{-4} at 72.31˚C
PABM1c	2.52	30.5	25.98	32.2	0.9674	1.39×10^{-4} at 82.04˚C
PABM2a	2.78	37.96	33.29	31.6	0.9725	1.61×10^{-4} at 70.9˚C
PABM2b	2.65	82.86	55.76	38.4	0.8459	1.51×10^{-4} at 92.25˚C
PABM2c	2.74	56.36	44.08	36.5	0.9918	1.32×10^{-4} at 76.00˚C
PABM3a	2.95	55.01	42.05	37	0.9421	1.40×10^{-4} at 70.62˚C
PABM3b	2.94	69.28	46.38	35.3	0.7492	1.57×10^{-4} at 76.94˚C
PABM3c	2	157.3	96.33	44.3	0.9178	1.46×10^{-4} at 77.88˚C

TABLE 6: Comparison of cross-link density and Tg by DMA of cross-link co-acrylate macromolecule

DMA, dynamic mechanical analysis; Tg, glass transition temperature

Life cycle analysis

Incorporating bio-based materials can significantly reduce the carbon footprint associated with a product. The Centrum voor Milieukunde Leiden (CML) procedure, along with the ML-IA database, provides a means to estimate the environmental impact caused by the product, particularly focusing on LCA. Another method employed to check the impact category is the IPCC 2021 method, implemented by the Intergovernmental Panel on Climate Change, where the CO_2 uptake is fully comprised. Additional reductions in CO_2 emissions can be achieved during the conversion of bio feedstock to resin, as well as during other related activities like usage and end-of-life disposal. Calculating the carbon footprint of this process is feasible using the LCA methodology, where the process carbon footprint for bio-based materials/products, based on ISO 14040 LCA standards methodology, typically outperforms those derived from petrochemical feedstocks.

Determining the bio (carbon) content of bio-based materials is essential, as they may contain either 100% biogenic carbon (new carbon) or a mixture of biogenic and fossil/petroleum-based carbon (old carbon), either physically, chemically, or biologically. Therefore, defining the bio-based content involves quantifying the amount of biogenic carbon present in the product. Biogenic carbons are those absorbed, stored, and later emitted by organic matter such as grasses, plants, and trees. Global warming potential (GWP) is expressed over a timeframe of 100 years (GWP100) and 500 years (GWP500) in terms of the generated greenhouse gases, in kilograms of CO_2 equivalent (kg CO_2-eq). The limitations in the CML-IA method comprise total impact assessments (fossil, biogenic, and land transformation), whereas in the IPCC 2021, we can have separate impact assessment in terms of fossil, biogenic, and land transformation, with its damage assessment impact also observed in kg CO_2-eq.

The macromolecules of different processes are being studied in Table *7* to observe the impact and damage assessment as global warming potential. The data were captured using SimaPro, PRé Sustainability software.

IPCC 2021 GWP500-fossil impact category describes the information about the timeframe of 500 years and the BM1a being higher renewable-based macromolecules comprise lower kgCO_2-eq as 1.68032.

Method	Impact Category	Unit	BM1a	BM2b	BM3c
CML-IA baseline V3.08/World 2000 – Impact assessment	Global warming (GWP100)	kg CO_2-eq	3.25767	3.087539	2.997155
IPCC 2021 GWP500 V1.01 – Impact assessment	GWP500 – fossil	kg CO_2-eq	1.68032	1.8903	1.98326
	GWP500 – biogenic	kg CO_2-eq	0.000458	0.000505	0.000526
	GWP500 – land transformation	kg CO_2-eq	1.342968	0.951723	0.763157
IPCC 2021 GWP500 V1.01 – Damage assessment	GWP500 incl. CO_2 biogenic	kg CO_2-eq	3.023746	2.842528	2.746943

TABLE 7: Impact and damage assessment

Conclusions

Bio-based hydroxyl-functionalized macromolecules were prepared with unsaturation in their backbone, through the reaction of SOFA, MAN, and TMP using three different processing methods with varying hydroxyl values. The PDI of processed macromolecules is directly related to their synthesis route. Processes "a" and "c" showed superior abrasion resistance, scratch resistance, and gloss retention due to the development of narrow MW distribution. The acrylic copolymer, with the complete replacement of hydroxy functional acrylate with newly synthesized hydroxy functionalized macromolecule, was tested as clear coats using aliphatic polyisocyanate (HDI trimer-Desmodur N3390), and the tests were conducted successfully. The finish coat from the resin PABM1a, upon curing with aliphatic polyisocyanate, displayed excellent functional characteristics. FTIR substantiated the formation of free hydroxyl functional groups as well as ester linkages in the macromolecule structure. GPC results displayed a high MW copolymer in conjunction with a PDI ranging from 7 to 19. DMA results showed the excellent efficiency of cross-linking interaction between NCO entities of polyisocyanates and the hydroxyl units of acrylic polyols. The polymer also had excellent adhesion properties and high scratch hardness, good impact resistance, strong abrasion resistance, and showed outstanding gloss retention after 1000 hours of UV exposure. The aforementioned findings suggest that this is a promising approach toward more bio-based decorative and protective coating systems.

Additional Information

Author Contributions

All authors have reviewed the final version to be published and agreed to be accountable for all aspects of the work.

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Disclosures

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