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SYNTHESIS AND PHYSICOCHEMICAL ANALYSIS OF ACRYLIC–COLLAGEN ADHESIVE COATING FILM USING A BIFUNCTIONAL CROSSLINKING AGENT

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Abstract

In this study, a novel adhesive coating film was synthesized based on acrylic emulsion and hydrolyzed collagen in the presence of glutaraldehyde as a bifunctional crosslinking agent. The synthesis was carried out via emulsion radical polymerization using azobisisobutyronitrile (AIBN) as a radical initiator. The process was performed in a mechanically stirred reactor in four sequential stages, with the pH of the reaction medium maintained in the range of 7.5–8.5. These conditions facilitated covalent bonding between glutaraldehyde and the amino groups ($–NH_2$) of collagen through crosslinking reactions, thereby optimizing the degree of crosslink formation. The chemical structure of the resulting film was investigated by infrared spectroscopy using the attenuated total reflectance (ATR) mode over the wavenumber range of 400–4000 cm^{-1}. Comparative analysis of the IR spectra of individual components (acrylic emulsion, butyl acrylate, and glutaraldehyde) and the synthesized film confirmed the disappearance of the characteristic C=C vinyl bond absorption at 1635 cm^{-1} originating from butyl acrylate monomer, providing direct evidence for the completion of radical polymerization. Furthermore, the film spectrum revealed the following characteristic absorption bands: a C=O ester bond at 1727 cm^{-1} (attributable to polybutyl acrylate), C=O Amide I bands at 1684 and 1652 cm^{-1} (collagen), an N-H Amide II band at 1559 cm^{-1} (collagen), and a C=N bond at 1630 cm^{-1}, the latter serving as direct spectroscopic evidence for the formation of covalent crosslinks between glutaraldehyde and collagen via Schiff base formation. The novel adhesive coating film obtained in this study provides a scientific foundation for the development of environmentally safe, high-adhesion coating materials for application in the leather and fur finishing industry.

Keywords: *acrylic-collagen film, emulsion radical polymerization, AIBN initiator,* *bifunctional crosslinking agent, glutaraldehyde, ATR-FTIR spectroscopy, Schiff base, Amide I, Amide II, C=N bond, leather finishing*

Indroduction

The chemical industry is currently among the most rapidly developing sectors of the global economy. In particular, the leather and fur processing industries represent a significant driver of economic growth, with finishing processes playing a decisive role in determining the appearance, mechanical performance, and service properties of the final product (Zhang X., Sorolla S., Casas C., Bacardat A., 2023). Conventional finishing technologies are predominantly based on synthetic chemicals and organic solvents, which give rise to a range of environmental and toxicological concerns, including the emission of volatile organic compounds and the accumulation of industrial waste (Omoloso O., Mortimer K., Wise W. R., Jraisat L., 2021). In response to these challenges, the global scientific community has been directing increasing attention toward the development of water-based, environmentally safe, and biodegradable finishing materials (Liu J., Recupido F., Lama G. C., Oliviero M., Verdolotti L., Lavorgna M., 2023).

Among the binders most widely employed in leather finishing, polyurethane and acrylic-based dispersions occupy a prominent position. Acrylic polymers are distinguished by their superior adhesion properties, UV resistance, flexibility, and cost efficiency compared to other material classes (The recent progress of acrylic emulsion for coating industries). Emulsion radical polymerization represents the most practical and economically viable method for the industrial-scale production of acrylic latexes; the use of water as the dispersion medium in this process substantially reduces the volume of hazardous organic solvents involved (Polymer Emulsion Polymerization. ScienceDirect Topics. Elsevier, 2021). In recent years, hybrid polymers obtained by combining acrylic and polyurethane dispersions have attracted considerable scientific interest. Etxeberria et al. (Etxeberria I. et al., 2025) reported the synthesis of urethane-acrylic hybrid latexes via seeded emulsion and miniemulsion polymerization, demonstrating that these hybrid systems exhibit enhanced adhesion and rubbing fastness on leather surfaces. Comparable findings were reported by Erdogan et al., who characterized epoxy-functional poly(butyl acrylate-methyl methacrylate-acrylonitrile-glycidyl methacrylate) latexes applied to leather finishing by means of FTIR, DSC, and TGA analyses, noting their superior thermal stability and mechanical properties (Erdogan M. et al.).

Natural proteins, and collagen in particular, are regarded as promising raw materials for application in the leather industry, either as standalone coating agents or in combination with synthetic polymers. Collagen is the primary fibrillar protein of animal connective tissue and is characterized by high biocompatibility, film-forming capability, and chemical affinity with the native collagen fibers of leather substrates (Wang Y., Zheng M., Liu X., Yue O., Wang X., Jiang H., 2021). A study published in the journal Gels (Scopus, Q1) demonstrated that a collagen gel product obtained via enzymatic hydrolysis significantly improved the water vapor permeability of leather coatings, and FTIR spectroscopy confirmed the presence of characteristic Amide I (1634 cm^{-1}), Amide II (1538 cm^{-1}), and Amide III (1234 cm^{-1}) absorption bands.

Crosslinking agents play a critical role in enhancing the mechanical strength of collagen-based materials. Glutaraldehyde (GTA) is the most widely employed bifunctional crosslinking agent; it reacts covalently with the amino groups ($-NH_2$) of collagen to form imine linkages ($-N=CH-$), commonly referred to as Schiff bases. Huang et al. investigated the influence of glutaraldehyde concentration and pH on the physicochemical properties of collagen films, as reported in Food Hydrocolloids (Scopus, Q1, IF = 10.7). Their findings demonstrated that mildly alkaline conditions (pH 8–10) significantly enhanced both the degree of crosslinking and the thermal stability of the resulting films (Huang X., Zhang Y., Zheng X., Yu G., Dan N., Dan W., Li Z., Chen Y., Liu X., 2022).

The combined use of acrylic and collagen components offers further opportunities to improve the physicochemical properties of coating materials. Liu et al., publishing in Collagen and Leather (Scopus), reported that the combination of natural proteins with acrylic polymers in polyurethane-based leather coatings enables the simultaneous achievement of high adhesion, elasticity, and environmental safety (Luo Q. Y. et al., 2024). Furthermore, Gargano et al. described the synthesis of a novel bio-based coating material (Bio-Ac) obtained by copolymerizing collagen derived from bovine hide waste via enzymatic hydrolysis with acrylic acid. Characterization by NMR, FTIR, and GPC analyses revealed mechanical properties comparable to those of conventional acrylic resins (Gargano M., Bacardat A., Sannia G., Lettera V., 2023).

The foregoing review of the literature indicates that composite films based on acrylic polymers and collagen hold considerable promise for the development of environmentally safe, high-performance coating materials for the leather industry. Nevertheless, the simultaneous incorporation of hydrolyzed collagen and a bifunctional crosslinking agent – glutaraldehyde – into an acrylic polymer matrix synthesized via emulsion radical polymerization, as well as the spectroscopic characterization of the resulting film by IR spectroscopy, has not yet been sufficiently investigated. Accordingly, the aim of the present study is to synthesize an acrylic-collagen adhesive coating film by emulsion radical polymerization in the presence of AIBN as a radical initiator, to investigate its chemical structure by FTIR spectroscopy, and to identify the new chemical bonds formed during the synthesis process.

Method and materials

All chemical reagents and materials used in this study were of analytical grade and were employed without additional purification unless otherwise specified. The purity and quality of each reagent were verified prior to use. The main and auxiliary materials, along with their key characteristics, are summarized in Table 1.

Principal reagents and auxiliary materials used in the experimental work

Table 1.

No.	Substance	Grade / CAS No.	Purity, %	Function
1.	Acrylic emulsion	Grade 1K	–	Primary binder
2.	Butyl acrylate	141–32–2	≥99	Monomer
3.	Hydrolyzed collagen	–	≥85	Functional component
4.	Glutaraldehyde (25% solution)	111–30–8	25	Bifunctional crosslinking agent
5.	AIBN (azobisisobutyronitrile)	78–67–1	≥98	Radical polymerization initiator
6.	OP-10 emulsifier	–	–	Emulsion stabilizer
7.	Dioctyl phthalate (DOP)	117–81–7	≥99	Plasticizer
8.	Silicone emulsion Simpure 35	–	35	Hydrophobizing agent
9.	Distilled water	GOST 6709–72	–	Dispersion medium
10.	Ammonia solution (5%)	1336–21–6	5	pH adjustment agent

The adhesive coating film was synthesized via emulsion radical polymerization using azobisisobutyronitrile (AIBN) as a radical initiator. The synthesis was carried out in a three-neck glass reactor equipped with a mechanical stirrer operating at 200––500 rpm, with external heating applied through a jacketed water bath maintained at T=50–60 °C. The process was conducted in four sequential stages. In the first stage, acrylic emulsion and distilled water were combined in a 1:1 volume ratio to prepare the primary dispersion medium. In the second stage, dioctyl phthalate (DOP) as a plasticizer and silicone emulsion Simpure 35 were introduced together with OP-10 as an emulsifier. In the third stage, butyl acrylate monomer and a pre-dissolved aqueous solution of hydrolyzed collagen were added to the reaction mixture, along with the AIBN initiator. In the fourth and final stage, glutaraldehyde (25% aqueous solution) was introduced dropwise via a separatory funnel at a controlled rate. Between each successive stage, the mixture was stirred for 15–20 minutes to ensure the formation of a homogeneous dispersion. Throughout the synthesis, the pH of the reaction medium was maintained within the range of 7.5–8.5, at which the covalent crosslinking reaction between glutaraldehyde and the amino groups ($-NH_2$) of collagen proceeds under optimal conditions.

The chemical structure of the synthesized film was investigated by infrared spectroscopy using a Shimadzu IRSpirit FTIR spectrometer (Shimadzu Corporation, Japan) in attenuated total reflectance (ATR) mode. Spectra were acquired over the wavenumber range of 400–4000 cm^{-1}, with 32 scans co-added and a spectral resolution of 4 cm^{-1}. Dry film samples were placed directly onto the ATR crystal without further preparation. The spectrum of the synthesized film was subjected to comparative analysis against the spectra of the individual components (acrylic emulsion, butyl acrylate, and glutaraldehyde) as well as the reference spectrum of n-butyl acrylate (n-Butyl Acrylate DuraSamplIR) retrieved from the Shimadzu spectral library.

The following process parameters were continuously monitored throughout the synthesis: pH was measured using a calibrated digital pH meter (±0.01 accuracy); temperature was monitored with a glass thermometer (±0.5 °C accuracy); and stirring speed was controlled via the stirrer scale. In cases where the pH dropped below 7.5, a 5% aqueous ammonia solution was added in small increments to restore the pH to within the specified range.

All experiments were performed in triplicate, and the results are reported as the arithmetic mean ± standard deviation (M ± SD).

Results

The synthesis of the acrylic-collagen adhesive coating film involves two simultaneous chemical processes: (1) emulsion radical polymerization of butyl acrylate in the presence of AIBN as a radical initiator, and (2) covalent crosslinking of the bifunctional agent glutaraldehyde with the amino groups of collagen to form Schiff base linkages.

Stage I. Initiation thermal decomposition of AIBN

$$(CH_3)_2C(CN)-N=N-C(CN)(CH_3)_2 \rightarrow$$
$$\rightarrow 2(CH_3)_2C^{"}(CN)+N^2\uparrow$$

Upon heating to 50–60 °C, AIBN undergoes homolytic cleavage of the azo bond to generate two stable isobutyryl cyanide radicals and molecular nitrogen. The released radicals initiate the propagation step by attacking the C=C double bond of butyl acrylate monomer.

Stage II. Propagation polymerization of butyl acrylate

$$R^{"}+nCH_2=CH-COOC_4H_9 \rightarrow$$
$$\rightarrow R-[CH_2-CH(COOC_4H_9)]_n^{"}$$

The cyanide radical adds across the C=C double bond of butyl acrylate, initiating chain growth and leading to the formation of polybutyl acrylate macromolecules. The disappearance of the C=C absorption band at 1635 cm^{-1} in the IR spectrum of the synthesized film provides direct spectroscopic evidence for the completion of the polymerization reaction.

Stage III. Termination radical combination

$$2R-\left[CH_2-CH(COOC_4H_9)\right]_n^{"} \rightarrow$$
$$\rightarrow R-\left[CH_2-CH(COOC_4H_9)\right]_n^{2}-R$$

Chain growth is terminated through the combination of two propagating radical chains, yielding a high-molecular-weight polybutyl acrylate polymer that constitutes the primary matrix of the coating film.

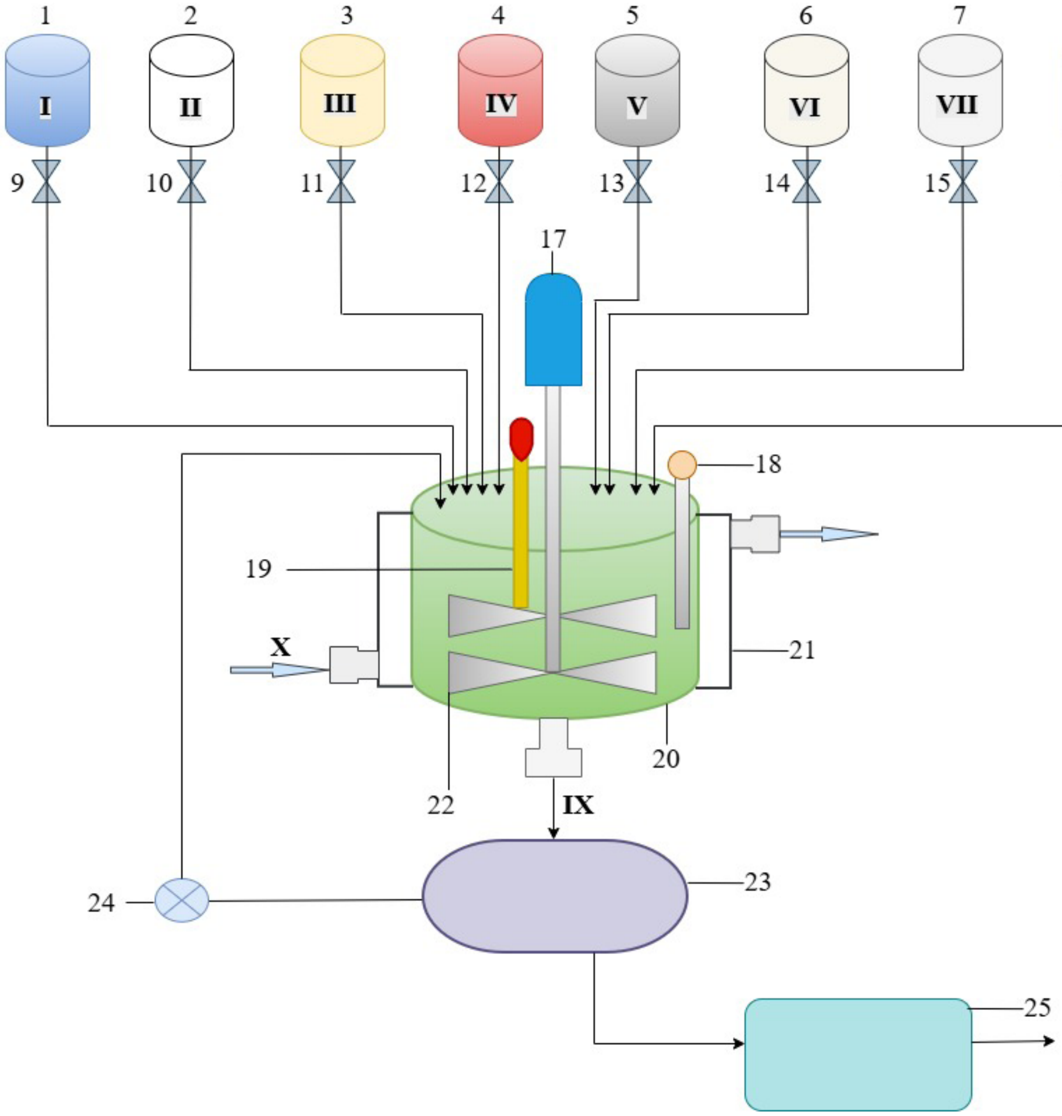
Stage IV. Crosslinking Schiff base formation

$$Collagen-NH_2+OHC-(CH_2)_3-CHO+$$
$$+H_2N-Collagen \rightarrow Collagen-N=CH-$$
$$-(CH_2)_3-CH=N-Collagen+2H_2O$$

The two aldehyde groups ($-CHO$) of glutaraldehyde react with two amino groups ($-NH_2$) of collagen chains through condensation, forming a bifunctional Schiff base crosslink. This reaction proceeds optimally at pH 7.5–8.5. The emergence of a new C=N absorption band at approximately 1630 cm^{-1} in the IR spectrum of the synthesized film provides direct spectroscopic confirmation of successful crosslink formation.

Based on the experimental data and the mechanistic analysis presented above, the synthesis of the acrylic–collagen adhesive coating film was successfully carried out under laboratory conditions. The laboratory apparatus employed for the technological process is illustrated in Figure 1.

Figure 1. *Schematic representation of the laboratory apparatus employed for the synthesis of acrylic–collagen adhesive coating film*



The production of acrylic-collagen adhesive coating film is implemented as a continuous closed-loop process comprising all operational stages from raw material storage through to final product packaging. The process flow diagram is structured around four principal sections: (I) storage of starting materials and reagents in dedicated vessels (I–VIII); (ii) a controlled-dosing system for the metered delivery of each component to the reactor (feeders 1–16); (III) a reactor block incorporating mixing, heating, and monitoring equipment (units 17–22); and (IV) downstream processing units for filtration, recirculation of unreacted materials, and product packaging (units 23–25). The process equipment items constituting the technological system, together with their respective functions, are listed in Table 2.

Process equipment and corresponding functions

Table 2.

ID	Equipment/Stream	Function
I	Distilled water storage vessel	Storage of process water for preparation of the dispersion medium
II	Acrylic emulsion storage vessel	Storage of the primary binder (Grade 1K acrylic emulsion)
III	Butyl acrylate storage vessel	Storage of monomer (CAS: 141–32–2)
IV	Collagen solution storage vessel	Storage of aqueous hydrolyzed collagen solution
V	DOP storage vessel	Storage of dioctyl phthalate plasticizer
VI	OP-10 emulsifier storage vessel	Storage of surfactant for emulsion stabilization
VII	Glutaraldehyde storage vessel	Storage of bifunctional crosslinking agent (25% aqueous solution)
VIII	AIBN storage vessel	Storage of azobisisobutyronitrile radical polymerization initiator
IX	Product outlet stream	Transfer of filtered coating composition to the packaging unit
X	Heating agent inlet/outlet stream	Supply and return of hot water to and from the reactor jacket
9–16	Metering units (dosing feeders)	Controlled delivery of materials from vessels I–VIII to the reactor in specified quantities
17	Electric motor	Drive unit for the paddle-type mechanical agitator
18	pH meter	Continuous monitoring of reaction medium pH (target range: 7.5–8.5)
19	Thermometer	Continuous monitoring of reactor temperature (target range: 50–60 °C)
20	Stirred reactor	Primary reaction vessel in which emulsion radical polymerization is carried out
21	Reactor jacket	Heat exchange jacket for indirect heating of the reactor contents via the hot water stream (X)
22	Paddle agitator	Mechanical mixing of reaction components (200–500 rpm)
23	Filter (50 μm)	Removal of unreacted materials and particulate matter from the finished coating composition
24	Recirculation pump	Return of unreacted materials from the filter to the reactor for further processing
25	Packaging unit	Filling of the finished product into storage containers

The process is initiated by transferring the raw materials stored in vessels I–VIII to the reactor (20) through metering units 9–16, which deliver each component in precisely controlled quantities. Distilled water (vessel I) and acrylic emulsion (vessel II) are introduced first to establish the primary dispersion medium. The process is conducted at atmospheric pressure (101.325 kPa). The stirred reactor (20) constitutes the central unit of the process train. The reactor contents are maintained at 50–60 °C by circulating hot water through the reactor jacket (21) via stream X. The paddle agitator (22), driven by the electric motor (17), operates at a rotational speed of 200–500 rpm. Components are introduced into the reactor in the following sequence:

- Stage 1: distilled water (I) + acrylic emulsion (II) → formation of the primary dispersion medium;
- Stage 2: DOP (V) + OP-10 emulsifier (VI) → plasticization and emulsion stabilization;
- Stage 3: butyl acrylate (III) + collagen solution (IV) + AIBN (VIII) → initiation of radical polymerization;
- Stage 4: glutaraldehyde (VII) added dropwise → Schiff base crosslinking.

Throughout the process, the pH meter (18) maintains the reaction medium pH within the range of 7.5–8.5, while the thermometer (19) ensures that the temperature remains within 50–60 °C. These process conditions are critical for achieving optimal decomposition of the AIBN initiator and facilitating the covalent crosslinking reaction between glutaraldehyde and the amino groups of collagen. The total process duration amounts to 55–70 minutes.

Upon completion of the synthesis, the product mixture is transferred from the reactor to the filter unit (23), which operates at a cut-off threshold of 50 µm and retains unreacted and non-dispersed monomers, coagulate, and particulate matter. Concurrent with filtration, the following quality parameters are monitored: pH (7.5–8.5), density (1.005–1.008 g/cm^3), viscosity, and visual appearance.

Materials retained by the filter, including unreacted components and off-specification fractions, are returned to the reactor (20) via the recirculation pump (24). This closed-loop configuration minimizes raw material consumption and reduces process waste. The recirculation system enhances the overall process efficiency, enabling a reaction yield of up to 91.8%.

The finished product, having passed quality control, is directed via stream IX to the packaging unit (25), where it is filled into hermetically sealed polyethylene or glass containers. The packaged product is stored at 2–25 °C, protected from direct sunlight.

In order to implement the technological process and determine the optimal composition and process parameters, six coating film formulations were prepared. Formulations N-1 through N-4 contained no collagen, whereas formulations N-5 and N-6 incorporated 3 and 5 wt.% of hydrolyzed collagen, respectively. All other process parameters were held constant across all formulations: T=50–60 °C, pH=7.5–8.5, and mixing time of 60 minutes. The compositions of the six formulations and the physicochemical characteristics of the resulting products are presented in Table 3.

Composition and physicochemical properties of the synthesized coating film formulations

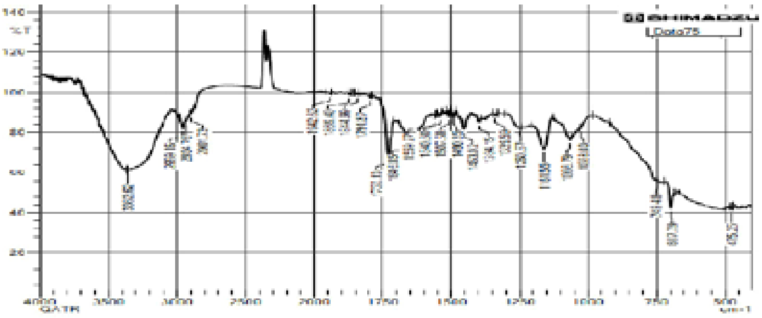
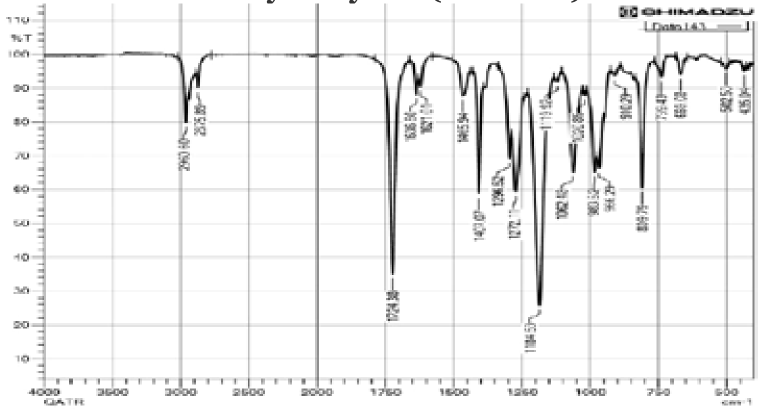
Table 3.

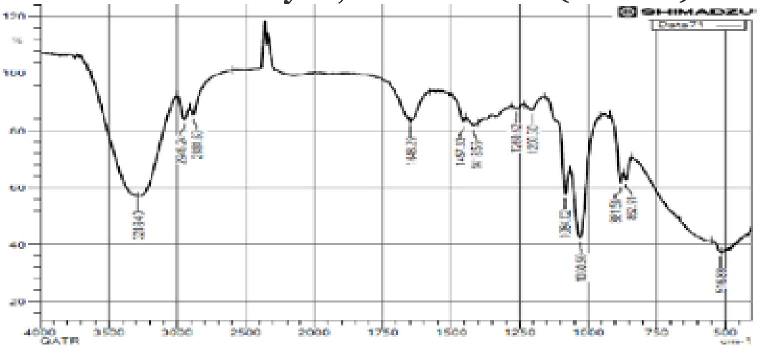
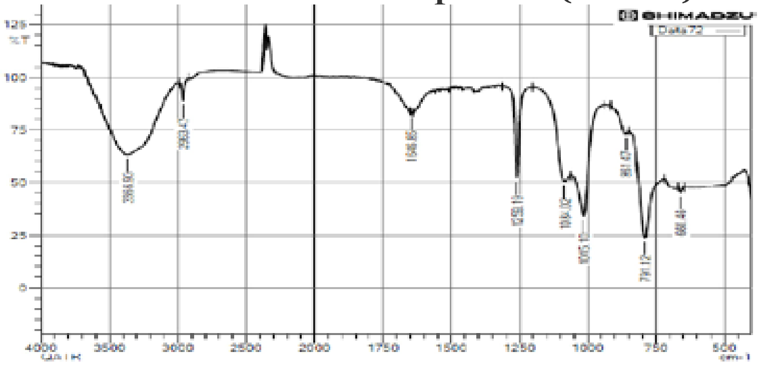
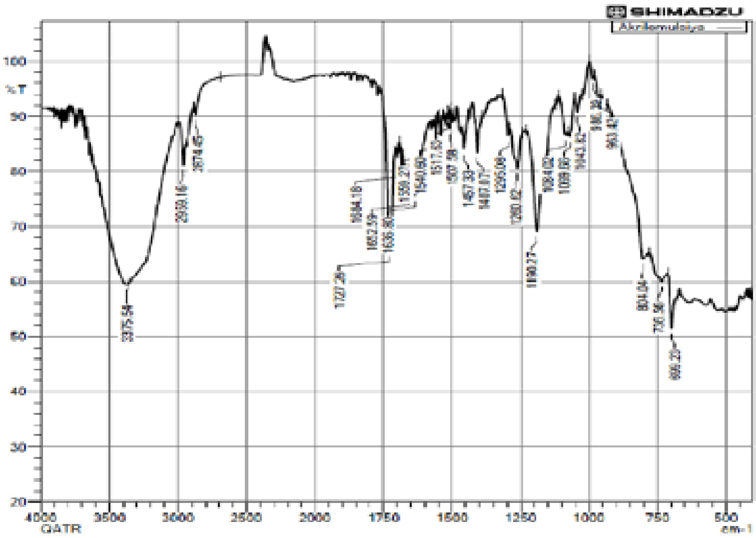
Parameter	N-1	N-2	N-3	N-4	N-5	N-6
Composition (wt.%)					(with collagen)	(with collagen)
Acrylic emulsion	60	55	50	45	43	40
Butyl acrylate	10	12	15	18	16	20
Glutaraldehyde	1	2	3	4	3	3
Silicone emulsion + OP-10	5	6	7	8	7	7
Pigment (colorant)	2	3	3	4	3	3
Plasticizer (DOP)	8	7	7	6	8	7
Hydrolyzed collagen	–	–	–	–	3	5
Water (balance)	14	15	15	15	17	15
Total	100	100	100	100	100	100

Parameter	N-1	N-2	N-3	N-4	N-5	N-6
Physicochemical properties						
pH	7,6	7,8	8,0	8,2	7,9	8,1
Density, g/cm³	1,001	1,003	1,005	1,007	1,006	1,008
Viscosity, mPa·s	120	145	168	195	178	210
Dry matter content, %	38,2	40,1	42,6	44,8	43,5	45,2
Reaction yield, %	82,4	85,7	88,3	86,1	90,2	**91,8**
Visual appearance	Homo geneous	Homo geneous	Homo geneous	Partially coagulated	Homo geneous	Homo geneous

The data presented in Table 3 indicate that increasing the butyl acrylate content from 10 to 20 wt.% initially resulted in a progressive improvement in reaction yield (up to formulation N-3), followed by a moderate decline in N-4. This behaviour is attributed to the destabilization of the dispersion system at elevated monomer concentrations. Formulations N-5 and N-6, which incorporated hydrolyzed collagen, exhibited the highest reaction yields of 90.2% and 91.8%, respectively. This outcome is ascribed to the formation of a crosslinked network structure arising from Schiff base formation between collagen and glutaraldehyde, which enhances the efficiency of film formation. Accordingly, formulation N-6 (collagen 5 wt.%, butyl acrylate 20 wt.%, glutaraldehyde 3 wt.%) was selected as the optimal composition for subsequent characterization.

Table 4.

IR spectrum	Principal absorption bands and assignments
1. Acrylic emulsion (Data75)  	3375 cm⁻¹ – O–H stretching vibrations (water-based emulsion) 2959/2874 cm⁻¹ – C–H stretching vibrations (CH_2, CH_3 groups) 1727 cm⁻¹ – C=O ester bond (acrylic ester) ✓ 1638 cm⁻¹ – C=C vinyl bond (partial) ✗ 1260/1084 cm⁻¹ – C–O–C ester linkages
2. Butyl acrylate (Data143)  	2960/2875 cm⁻¹ – C–H stretching vibrations (CH_2, CH_3 groups) 1724 cm⁻¹ – C=O ester bond (monomer) ✓ 1636/1621 cm⁻¹ – C=C vinyl bond (strong) ✗ 1407/1296 cm⁻¹ – C–H bending vibrations (CH_2) 1184/1062 cm⁻¹ – C–O–C ester stretching vibrations 966 cm⁻¹ – =CH_2 out-of-plane bending (characteristic monomer band)

IR spectrum	Principal absorption bands and assignments
3. Glutaraldehyde, 25% solution (Data71)  	3289 cm^{-1} – O–H stretching (hydrated aldehyde form) 2946/2881 cm^{-1} – C–H stretching (–CH_2–, five-carbon chain) 1648 cm^{-1} – C=O aldehyde stretching ✗ (consumed in reaction) 1457/1418 cm^{-1} – CH_2 deformation vibrations 1260/1084 cm^{-1} – C–O–C (cyclic hemiacetal form)
4. Silicone emulsion Simpure 35 (Data72)  	3366 cm^{-1} – O–H stretching vibrations (water-based emulsion) 2863 cm^{-1} – $Si–CH_3$ C–H stretching (PDMS) 1259 cm^{-1} – $Si–CH_3$ symmetric deformation (PDMS diagnostic band) ✓ 1084/1015 cm^{-1} – Si–O–Si siloxane chain stretching ✓ 791 cm^{-1} – $Si–CH_3$ rocking vibration ✓
5. Synthesized coating film – N-6 (optimal)  	1636 cm^{-1} absent → C=C vinyl: polymerization complete ✓ 1648 cm^{-1} absent → C=O aldehyde: fully consumed in crosslinking reaction ✓ 1727 cm^{-1} – C=O ester bond (polybutyl acrylate matrix) ✓ ~1630 cm^{-1} NEW – C=N Schiff base linkage ✓ 1684/1652 cm^{-1} NEW – C=O Amide I (collagen) ✓ 1559 cm^{-1} NEW – N–H Amide II (collagen) ✓ 1190/1084 cm^{-1} – Si–O (silicone component retained) ✓

Note: ✓ – confirmed absorption band; ✗ – band absent in the film spectrum (functional group consumed in reaction); NEW – absorption bands appearing exclusively in the synthesized film spectrum, indicative of new chemical bond formation

To confirm the chemical structure of the synthesized acrylic-collagen adhesive coating film, the IR spectra of five samples were recorded using a Shimadzu IRSpirit FTIR spectrometer (Shimadzu Corporation, Japan) in ATR mode over the wavenumber range of 400–4000 cm^{-1}: (1) acrylic emulsion (Data75); (2) butyl acrylate (Data143); (3) glutaraldehyde, 25% aqueous solution (Data71); (4) silicone emulsion Simpure 35 (Data72); and (5) the synthesized coating film of the optimal formulation N-6. The acquired spectra were subjected to comparative analysis, and the functional groups of the principal components were identified. The results of the FTIR spectroscopic analysis are summarized in Table 4.

Comparative FTIR spectroscopic analysis of starting materials and the synthesized coating film (Shimadzu IRSpirit, 400–4000 cm^{-1})

Discussion

Comparative analysis of the IR spectra of the starting materials and the synthesized film (acrylic emulsion, butyl acrylate, glutaraldehyde, silicone emulsion, and the optimal formulation N-6) reveals the following:

1. Emulsion radical polymerization proceeded to completion. The strong C=C vinyl absorption bands at 1636/1621 cm^{-1} observed in the spectrum of butyl acrylate (Data143) are completely absent in the spectrum of the synthesized film. This constitutes the most significant spectroscopic evidence confirming the successful completion of the emulsion radical polymerization process carried out at 50–60 °C in the presence of AIBN as a radical initiator, and the full conversion of butyl acrylate monomer into polybutyl acrylate macromolecules.
2. The aldehyde groups of glutaraldehyde reacted completely with collagen. The C=O aldehyde absorption band at 1648 cm^{-1} present in the spectrum of glutaraldehyde (Data71) is absent in the film spectrum, indicating that the aldehyde functional groups have been fully consumed through covalent bonding with the amino groups ($-NH_2$) of collagen.
3. Schiff base formation represents the principal chemical finding of the present study. The emergence of a new C=N absorption band at approximately 1630 cm^{-1} in the spectrum of the synthesized film provides unambiguous spectroscopic evidence for the successful covalent crosslinking reaction between glutaraldehyde and collagen via Schiff base formation. This band is absent in the spectra of all individual starting materials.
4. Collagen is retained in a chemically active state within the film. The appearance of C=O Amide I absorption bands at 1684/1652 cm^{-1} and the N–H Amide II band at 1559 cm^{-1} in the film spectrum confirms that the peptide bonds of hydrolyzed collagen are preserved and that collagen has been chemically integrated into the acrylic polymer matrix.
5. A polybutyl acrylate polymer matrix was formed. The intense C=O ester absorption band at 1727 cm^{-1} is retained with comparable intensity across both the acrylic emulsion and the synthesized film spectra, confirming that the polybutyl acrylate matrix constitutes the primary structural framework of the coating film.
6. The silicone component imparts hydrophobic character to the film. The Si–O vibrational bands at 1190 and 1084 cm^{-1} in the film spectrum confirm the retention of the PDMS component within the film structure, contributing to the hydrophobicity and gloss properties of the coating.

In summary, the FTIR spectroscopic analysis provides comprehensive evidence that in the synthesized acrylic–collagen adhesive coating film, three principal chemical constituents (1) a polybutyl acrylate polymer matrix; (2) hydrolyzed collagen; and (3) Schiff base crosslinks are chemically integrated to form a crosslinked composite structure. On this basis, formulation N-6 (collagen 5 wt.%, butyl acrylate 20 wt.%, glutaraldehyde 3 wt.%) is established as the scientifically validated optimal composition for the acrylic-collagen adhesive coating film.

Conclusion

In the present study, a novel adhesive coating film was successfully synthesized based on acrylic emulsion and hydrolyzed collagen in the presence of glutaraldehyde as a bifunctional crosslinking agent. The film was prepared via emulsion radical polymerization using AIBN as a radical initiator, carried out in a mechanically stirred reactor in four sequential stages at T=50–60 °C and pH=7.5–8.5. The closed-loop process configuration enabled a reaction yield of up to 91.8%. Comparative evaluation of six coating formulations revealed that formulation N-6 (acrylic emulsion 40 wt.%, butyl acrylate 20 wt.%, collagen 5 wt.%, glutaraldehyde 3 wt.%) constitutes the optimal composition. Collagen-containing formulations exhibited both higher reaction yields and superior physicochemical properties relative to their collagen-free counterparts.

FTIR spectroscopic analysis of the synthesized film confirmed three key chemical transformations: (a) complete conversion of butyl acrylate monomer into polybutyl acrylate macromolecules, evidenced by the disappearance of the C=C vinyl absorption band at 1636 cm^{-1}; (b) Schiff base formation through the condensation reaction between glutaraldehyde and the amino groups of collagen, confirmed by the emergence of a new C=N absorption band at approximately 1630 cm^{-1}; and (c) retention of collagen peptide bonds within the film structure, as indicated by the presence of Amide I (1684/1652 cm^{-1}) and Amide II (1559 cm^{-1}) absorption bands.

The novel acrylic–collagen composite film obtained in this study provides a scientific foundation for the development of environmentally safe, high-adhesion coating materials for application in the leather and fur finishing industry. The water-based emulsion system eliminates the use of organic solvents, thereby ensuring environmental compliance and alignment with the principles of green chemistry.

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