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# EFFECTS OF CASEIN AND ISOCYANATE CONCENTRATIONS AS CROSSLINKERS IN THE FINISHING PROCESS OF GOAT LEATHER FOR SHOE UPPERS

***Nais Pinta Adetya[1*], Nur Mutia Rosiati[1], Sofwan Siddiq Abdullah[1], Emiliana Anggriyani[1], Laili Rachmawati[1], Mustafidah Udkhiyati[1], Abimanyu Yogadita Restu Aji[2], Ikmal Khalala[1]***

[1]Department of Leather Processing Technology, Politeknik ATK Yogyakarta, Yogyakarta 55188, Indonesia
[2]Department of Leather Product Processing Technology, Politeknik ATK Yogyakarta, Yogyakarta 55188, Indonesia

*Corresponding author: naispinta26@gmail.com

***Abstract***

*This study aimed to investigate the interaction between casein, used as a crosslinker, and binders in the leather coating process and to evaluate the quality of leather produced using casein crosslinkers compared with conventional isocyanate crosslinkers. The research methodology consisted of three stages: preparation and characterization of the crosslinkers, finishing of crust goat leather, and final testing. The FTIR spectrum of casein indicated the presence of stretching vibrations associated with functional groups related to coating performance. Leather quality was evaluated through color fastness to rubbing and leather softness tests. From a chemical reaction perspective, casein shows potential as a crosslinker when used in combination with isocyanate crosslinkers. PUD binders do not directly form covalent bonds with casein through –OH groups under normal conditions; however, strong physical interactions through hydrogen bonding can occur. In the presence of a crosslinker such as isocyanate, covalent reactions may take place, forming a stronger urethane/urea network. The rubbing fastness of all leather samples, except C1 (10 parts casein) and I3 (30 parts isocyanate), met the SNI standard.*

***Keywords:*** *Casein, crosslinker, finishing, goat leather, isocyanate*

## Introduction

The leather tanning process consists of four main stages: beamhouse operations, tanning, post-tanning, and finishing. Each stage has a specific purpose [1]. The finishing process is the final stage in leather tanning and provides an attractive appearance suitable for manufacturing various leather products [2]. Finishing also forms a protective layer that safeguards leather from water stains, scratches, and damage caused by moisture or temperature changes [3].

The main materials used in the finishing process include solvents, binders, dyes, and additives such as penetrators, fillers, and crosslinkers. Binders are the primary film-forming materials in leather finishing. They bind pigments and other components, forming a coherent film that adheres to the leather substrate [4]. Common binders used in leather finishing

include polyurethane, polyacrylic, nitrocellulose, and casein [5]. Casein is also used as a main binder, particularly for exotic skins such as monitor lizard and snake skins [6].

Crosslinkers are important additives in the coating industry and are widely used to enhance the chemical and mechanical resistance of coating systems, as well as to improve adhesion [7]. This is attributed to the formation of a continuous three-dimensional network, which can be formed by the crosslinker itself or through reactions between the crosslinker and the binder [8].

Crosslinkers used in the leather industry include isocyanates, carbodiimides, and aziridines [7]. The formation of crosslinks between hydroxyl (–OH) groups in polyurethane binders and –NCO groups in isocyanate crosslinkers results in strong crosslinked structures [9]. However, due to their reactive functional groups, crosslinkers can be hazardous, irritating, sensitizing, or even toxic to humans and the natural environment, depending on the type of reactive group, molecular weight, and ability to penetrate living cells [8]. Polyaziridines are classified as toxic, with a potential oral lethal dose of 5 × 50 mg/kg [10]. In addition, these crosslinking agents are not yet widely available in the local industry.

Several studies have investigated alternatives to conventional crosslinking agents, such as enzymes and acrylic epoxy systems [11] [10]. One material with potential as an alternative crosslinker is casein. Currently, in leather finishing processes, casein is commonly used as a binder, particularly for reptile leathers that employ glazing processes.

Moreover, casein is a bio-based material with lower toxicity compared with some conventional crosslinkers [10]. The amide groups in casein can react with isocyanate groups in polyurethane systems, which may affect the strength and durability of the finishing layer [12]. However, the application of casein as a crosslinker in polyurethane-based leather finishing systems has not been extensively studied, particularly regarding its interaction with polyurethane binders and its influence on the performance of the finishing layer.

## Experimental Section

### Materials

The material used in this study was crust goat leather for shoe uppers. The chemicals employed included water, surfactant (Pulcra), adhesive (Stahl), acrylic binder (Stahl), polyurethane dispersion (PUD; Stahl), pigments (Allied Chemicals), wax filler (Stahl), bovine milk casein (Sigma-Aldrich), isocyanate (Stahl), silicone emulsion (Stahl), and ammonium hydroxide (technical grade, 25% $NH_3$), obtained from a local industrial supplier in Yogyakarta, Indonesia. The equipment used in this study included a digital balance, measuring cylinders, stirrers, plastic beakers, trays, a stopwatch, a padding machine, a spray gun unit, a compressor, an inclined table, a measuring machine, a plating machine, knives/cutters, droppers, and filters. The instruments used for testing and characterization included an FTIR spectrometer (PerkinElmer Spotlight 400 Frontier), a crockmeter, and a leather softness tester.

### Preparation and Characterization of Crosslinkers

Casein exhibits low solubility; therefore, its solubility was enhanced by the addition of a base and heating. Casein dissolves under alkaline conditions through the formation of sodium caseinate. One gram of casein powder was dissolved in 10 mL of ammonium hydroxide, followed by stirring at 50°C until a homogeneous solution was obtained. A conventional isocyanate crosslinker, FX 0750, was used for comparison. Subsequently, both the casein and isocyanate crosslinkers were characterized using Fourier-transform infrared spectroscopy (FTIR) to identify the functional groups present in each crosslinker.

**Finishing Process of Crust Goat Leather**

Seven pieces of crust goat leather with a total area of 35 square feet (sq ft), where 1 sq ft = 0.093 $m^2$, were used in this study. Conditioning, staking, and toggling were first carried out to prepare the leather prior to the finishing process. The finishing process consisted of three stages: the first coat, the second coat, and the third coat. All stages were applied using a gravity-type spray gun, with a material application rate of approximately 10–15 g/sq ft. The process formulations are presented in Table 1.

The materials used in the first layer consisted of polyurethane adhesive and acrylic resin as binders, together with pigments, fillers, and water as the solvent. In the second layer, the polyurethane adhesive was replaced by a medium-soft polyurethane binder used in a higher amount. In addition, the pigment content in the second layer was higher than that in the first layer to maximize defect coverage. In the third layer, a silicone emulsion, a hard polyurethane binder, and isocyanate and casein crosslinkers were applied, with the crosslinker content varied from 10 to 30 parts. The final stage involved a mechanical plating process conducted at a temperature of 95°C, a pressure of 5 MPa, and a processing time of 3 seconds.

**Final Testing**

Functional group characterization of the crosslinker materials was carried out using FTIR. The leather samples produced in this study were evaluated through color fastness to rubbing and leather softness tests, which were conducted at the Testing Laboratory of Politeknik ATK Yogyakarta.

The rubbing fastness test was carried out in several stages. Two leather samples measuring 22 × 3 $cm^2$ were prepared, consisting of one sample for the dry rubbing test and one sample for the wet rubbing test. The samples were mounted on a crockmeter. A piece of white cotton cloth measuring 3 × 3 $cm^2$ was attached to the rubbing finger of the instrument. Two pieces of cloth were used: one dry and one moistened with distilled water. The crockmeter was operated and set to perform 10 rubbing cycles within 10 seconds. After rubbing, the cotton cloth was evaluated by comparing the staining level with the grey scale.

Leather softness testing was conducted using a softness meter equipped with a 25-mm ring. The leather sample was placed on the softness meter, and measurements were taken three times at different points on the sample.

**Table1.** Formulation of Goat Leather Finishing

| Chemicals | 1st coat (parts) | 2nd coat (parts) | 3rd coat (parts) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | I1 | I2 | I3 | C1 | C2 | C3 | IC1 |
| Water | 500 | 425 | 490 | 490 | 490 | 490 | 490 | 490 | 490 |
| PUD (adhesive) | 100 | - | - | - | - | - | - | - | - |
| Filler | 100 | 75 | - | - | - | - | - | - | - |
| Pigment | 75 | 100 | - | - | - | - | - | - | - |
| Acrylic binder | 225 | 150 | - | - | - | - | - | - | - |
| PUD (medium soft) | - | 250 | - | - | - | - | - | - | - |
| Silicone emulsion | - | - | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| PUD (hard) | - | - | 490 | 480 | 470 | 490 | 480 | 470 | 480 |
| Isocyanate* | - | - | 10 | 20 | 30 | - | - | - | 10 |
| Casein* | - | - | - | - | - | 10 | 20 | 30 | 10 |

## Results and Discussion

### Characterization Results of Casein and Isocyanate Crosslinkers

The bovine milk casein used in this study had a nitrogen content of 14.6%, according to the Sigma-Aldrich certificate of analysis for product number C7078. Functional group characterization of the crosslinker materials was carried out using FTIR. The results of the functional group characterization are presented in Figure 1.

The red spectrum represents the FTIR spectrum of the conventional crosslinker containing isocyanate (I), while the black spectrum represents the FTIR spectrum of the casein crosslinker (C). Based on the FTIR spectrum of isocyanate (I), the presence of isocyanate groups in the crosslinker was confirmed by a strong absorption peak at 2369 $cm^{-1}$ [10]. The FTIR spectrum of casein (C) showed stretching vibrations corresponding to O–H groups at 3430 $cm^{-1}$ and N–H groups at 3188 $cm^{-1}$ [14]. The amine ($–NH_2$) and hydroxyl (–OH) functional groups present in casein can act as reactive sites that form crosslinks with isocyanate (–NCO) groups, resulting in strong crosslinked networks that enhance the physical and chemical properties of the finishing layer [15] [16].

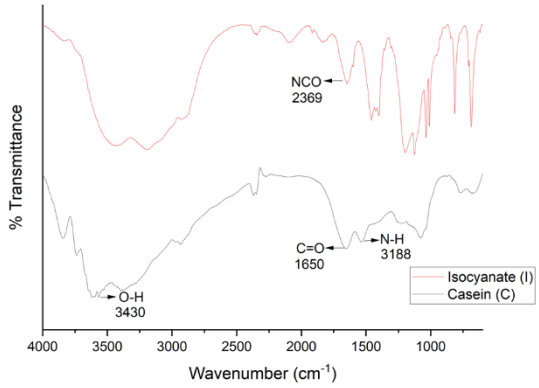


**Figure 1.** FTIR spectra of casein (C) and isocyanate (I)

### Effects of Casein and Isocyanate on Leather Rubbing Fastness

Rubbing fastness is an important parameter in the leather finishing process. In this study, the formulation varied the additives used in the top coat, namely the isocyanate crosslinker and the casein crosslinker. Isocyanates are additives commonly used as crosslinkers for binders. Crosslinkers play a significant role in finishing formulations because their use can influence coating rubbing fastness [8]. In leather finishing, casein typically functions as a primary binder, particularly for leathers subjected to mechanical glazing processes [17]. The results of the rubbing fastness test, evaluated using the grey scale for assessing staining, are presented in Table 2.

Based on Table 2, the rubbing fastness results of the top coat for samples using casein as an additive indicate that samples C2 and C3 met the requirements of SNI 0253:2009 for upper leather for footwear, particularly goat leather shoe uppers. However, sample C1, which contained 10 parts casein, exhibited a relatively low dry rubbing fastness value of 4 and did not meet the SNI standard for dry rubbing, which requires a minimum value of 4/5.

The binder used in this study was an aliphatic polyurethane dispersion (PUD). Aliphatic polyurethane dispersions are generally fully polymerized, meaning that the initial –NCO groups are no longer present [18]. PUDs are not reactive toward common functional groups unless they are modified with reactive moieties, such as isocyanate-containing components [19]. Therefore, under normal conditions, namely room temperature and neutral pH, the –OH groups in PUD do not spontaneously react

with the $-NH_2$ or –COOH functional groups of casein. Aliphatic PUDs do not form direct covalent bonds with casein through –OH groups under normal conditions. However, physical interactions through hydrogen bonding can occur between –OH/–NH groups in PUD and –COOH/$-NH_2$ groups in casein. These interactions can stabilize the film and enhance cohesion [20]. Since PUDs are fully reacted prepolymers, direct chemical reactions with casein are very limited, and hydrogen bonding is the dominant interaction mechanism [21], as illustrated in **Figure 2**.

**Table 2.** Results of the Color Rubbing Fastness Test

| Sample | Staining | | Remarks |
|---|---|---|---|
| | Dry | Wet | |
| C1 (10 parts casein) | 4 | 4/5 | Not compliant |
| C2 (20 parts casein) | 5 | 5 | Compliant |
| C3 (30 parts casein) | 5 | 5 | Compliant |
| I1 (10 parts isocyanates) | 5 | 5 | Compliant |
| I2 (20 parts isocyanates) | 4/5 | 5 | Compliant |
| I3 (30 parts isocyanates) | 4 | 5 | Not compliant |
| IC1 (10 parts isocyanate and casein) | 5 | 5 | Compliant |
| Standard (SNI 0253:2009) | 4/5 | 4 | |

The relative strength of chemical bonding as an adhesion mechanism in leather coatings strongly depends on the interfacial area between the leather and the finish. Nevertheless, chemical bonding is not considered the primary contributor to the adhesion of the finishing layer on leather. Although van der Waals forces, dipole interactions, and hydrogen bonding are generally regarded as weaker interactions than covalent bonds, the large number of such interactions over an extensive surface area can result in a significant overall effect [6].

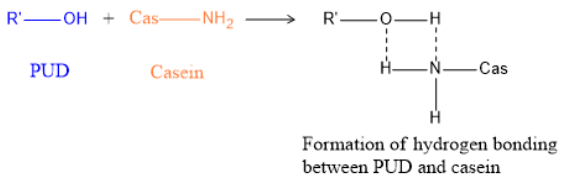


**Figure 2**. Hydrogen-bonding interactions between polyurethane dispersion binder and casein

Leather samples using conventional isocyanate crosslinkers, namely I1 and I2, exhibited high rubbing fastness values, with scores of 4/5 and 5, respectively, thus meeting the required standard. The formation of crosslinks between hydroxyl (–OH) groups in the polyurethane binder and –NCO groups in the isocyanate crosslinker results in strong crosslinked networks [9]. However, sample I3, which contained 30 parts of isocyanate crosslinker per 1,000 parts of formulation, showed dye transfer, particularly under dry rubbing conditions, with a value of 4. The amount of crosslinker significantly influences leather rubbing fastness, and there is no single dosage suitable for all conditions. This indicates that crosslinker use in finishing must be tailored to specific leather conditions [10]. The reaction between the PUD binder and the isocyanate crosslinker forms new urethane linkages, leading to increased hardness, chemical resistance, and scratch resistance [22]. The reaction between the PUD binder and the isocyanate crosslinker, forming new urethane bonds, is illustrated in **Figure 3.**

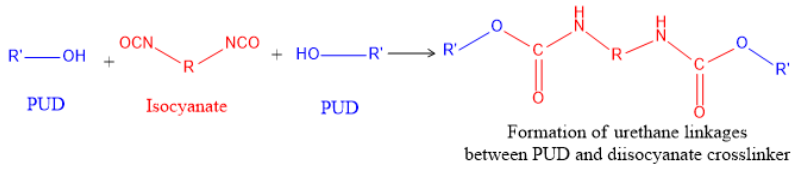


**Figure 3**. Formation of urethane linkages between polyurethane dispersion binder and isocyanate crosslinker

Aliphatic PUD does not form direct covalent bonds with casein through –OH groups under normal conditions. However, strong physical interactions through hydrogen bonding can occur, and in the presence of a crosslinker such as isocyanate, covalent reactions may take place, leading to the formation of stronger urethane/urea networks. This behavior is reflected in sample IC1, which employed both isocyanate and casein as crosslinking additives and exhibited a rubbing fastness value of 5 under both dry and wet conditions. The isocyanate groups present in the crosslinker within the binder can react with amino groups in casein. This reaction forms urea (–NH–CO–NH–) linkages or urethane linkages when hydroxyl groups are involved, resulting in a more strongly crosslinked network [23]. Such reactions generate a three-dimensional interpenetrating network between casein and polyurethane molecules, thereby enhancing the coating's resistance to solvents, abrasion, and temperature [22]. The formation of urethane linkages between carbamic acid species, derived from PUD–isocyanate reactions, and casein is illustrated in **Figure 4.**

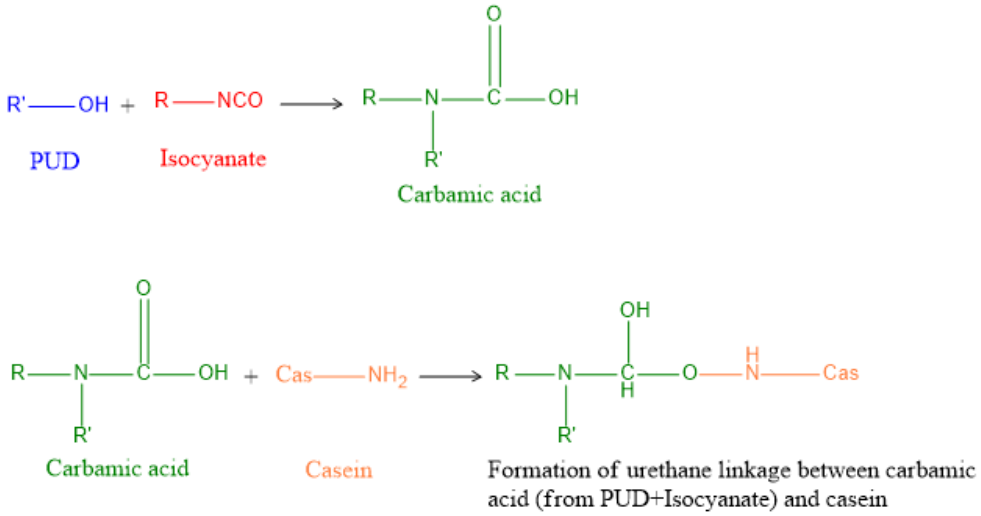


**Figure 4.** Formation of urethane linkages between carbamic acid species, derived from PUD–isocyanate reactions, and casein

## Effects of Casein and Isocyanate on Leather Softness

The use of crosslinkers has the potential to influence leather softness. Polyisocyanates are used to harden polyurethane through crosslinking reactions [9]. The results of leather softness testing using a 25-mm ring are presented in **Table 3**.

Based on the softness test results presented in Table 3, no significant difference was observed between the softness of crust leather and finished leather. This indicates that the use of crosslinkers, either casein or isocyanate, in

the finishing process of this study did not have a significant effect on leather softness. One of the most important processes influencing leather softness is fatliquoring [24]. The appropriate selection and application of oils during the fatliquoring process can significantly affect physical properties such as tear strength, stitch strength, tensile strength, and softness [25] [26].

**Table 3.** Results of Leather Softness Testing

| Sample | Softness (mm) | |
|---|---|---|
| | Crust Leather (mm) | Finished Leather (mm) |
| C10 | 2.3 | 2.2 |
| C20 | 2.4 | 2.4 |
| C30 | 2.8 | 2.6 |
| I10 | 2.7 | 2.6 |
| I20 | 2.1 | 2.2 |
| I30 | 2.6 | 2.5 |
| IC1 | 2.5 | 2.5 |

## Conclusion

The casein concentration that produced rubbing fastness values meeting the SNI standard was observed in sample C2 (20 parts), while the optimal isocyanate concentration was found in sample I1 (10 parts). The rubbing fastness of all leather samples, except C1 and I3, met the SNI standard. Furthermore, the use of either casein or isocyanate in all samples did not have a significant effect on leather softness.

Based on the experimental results, including the softness parameter, the combination of casein and isocyanate crosslinkers (IC1) showed performance comparable to that of the individual systems (C3 and I1), and this formulation met the SNI requirements. This indicates that casein can function in combination with isocyanate as part of a crosslinking system. However, since only one combination formulation was evaluated, further studies with broader formulation variations are needed to confirm its potential. Under normal conditions, the PUD binder does not form direct covalent bonds with casein through –OH groups; however, strong physical interactions through hydrogen bonding can occur. In the presence of a crosslinker such as isocyanate, covalent reactions may take place, leading to the formation of stronger urethane/urea networks.

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