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Effect of Phenol–Formaldehyde Molar Ratio on the Physicochemical Properties of Phenolic Synthetic Tanning Agent (Syntan)

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Abstract: Phenolic synthetic tanning agents (syntans) are widely used in the leather industry due to their controllable properties and consistent performance. This study aims to investigate the effect of phenol–formaldehyde molar ratio on the physicochemical properties of syntans synthesized via sulfonation.
The syntans were prepared using various molar ratios (0:1, 0.5:1, 1:1, 1.5:1, 1:0.5, and 1:0) through condensation followed by sulfonation. The products were characterized in terms of pH, specific gravity, viscosity, degree of sulfonation (DS), and functional groups using FTIR spectroscopy.
The results show that increasing phenol or formaldehyde concentration led to higher specific gravity and viscosity, indicating increased polymerization. The pH values ranged around ~4, confirming suitability for leather processing. The DS decreased with increasing phenol or formaldehyde concentration, suggesting competition between polymerization and sulfonation reactions. The optimal molar ratio (1:1) produced the most homogeneous and stable syntan system.
The pH values of all syntans were consistently around ~4, indicating suitability for leather processing. Increasing phenol or formaldehyde concentration resulted in higher viscosity and specific gravity, while the degree of sulfonation decreased significantly, confirming the trade-off between polymerization and sulfonation reactions. In conclusion, the phenol–formaldehyde molar ratio significantly influences syntan properties by controlling the balance between polymerization and sulfonation. These findings provide a scientific basis for optimizing syntan formulation and improving efficiency in sustainable leather processing.

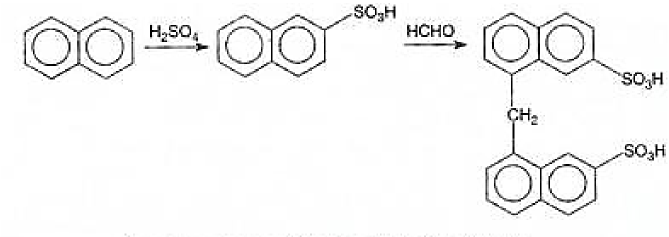
Keywords: Phenolic syntan; phenol–formaldehyde, synthetic tanning agent, sulfonation degree, physicochemical properties, leather processing.

Introduction

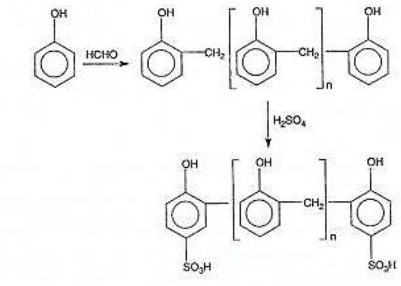
The leather processing industry relies heavily on chemical agents to enhance the stability, durability, and performance of collagen-based materials. Among these, tanning and retanning agents are essential for converting raw hides into functional leather with desirable mechanical and physical properties. Synthetic tanning agents, commonly known as syntans, have been developed as alternatives or supplements to traditional tanning materials, such as chrome salts and vegetable tannins. These syntans offer improved process control, tunable physicochemical properties, and consistent quality [3,2,1].
Phenolic syntans are an important class of synthetic tanning agents widely used in leather processing. They are synthesized through the condensation of phenol and formaldehyde, forming polymeric resins that are subsequently sulfonated to improve water solubility and

reactivity toward collagen fibers [7,6]. The chemical structure of phenolic syntans, including the distribution of hydroxyl and aromatic groups, governs their interaction with leather and influences key attributes such as grain smoothness, fullness, and flexibility.

The molar ratio of phenol to formaldehyde (F:P) is a critical factor in controlling polymerization. Under acidic conditions with phenol-rich compositions (F:P < 1), novolac-type structures are typically formed, whereas basic conditions with excess formaldehyde (F:P > 1) favor resol-type polymers [4,8].



Nerodol synthesis: sulfonation then polymerisation.



Novolak synthesis: polymerisation then sulfonation.

Figure 1. Synthesis route of phenolic syntan

These structural variations determine molecular weight, degree of branching, and crosslinking density, which directly affect properties such as viscosity, solubility, and penetration behavior of syntans in leather matrices.The polymerization mechanism of phenol–formaldehyde under different molar ratios is illustrated in Figure 2.

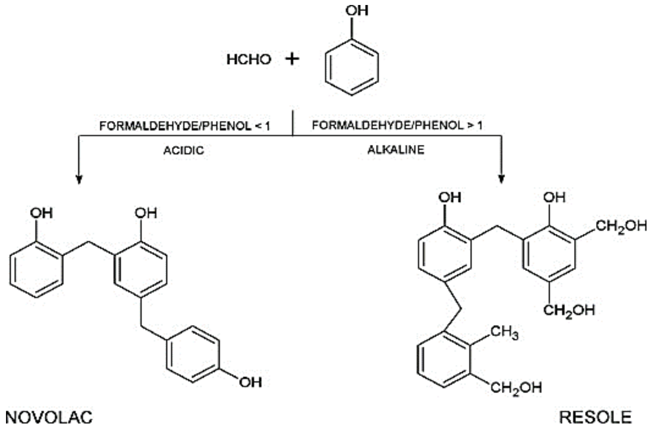


Figure 2. Polymerization mechanism of phenol–formaldehyde at different molar ratios

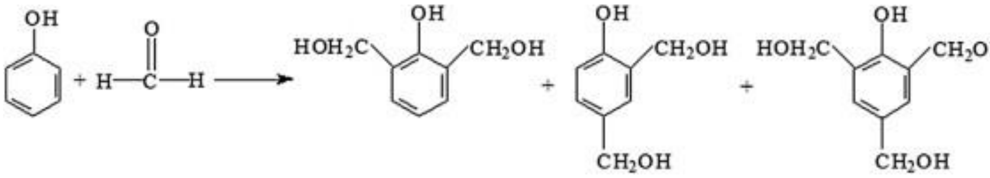


Figure 3. Formation of phenol–formaldehyde oligomers via ortho- and para-substitution

Sulfonation is a key modification step that introduces sulfonate (–SO_3H) groups into the aromatic polymer. This increases hydrophilicity, facilitates uniform dispersion in aqueous systems, and enhances penetration into collagen fibers. The chemical structure of sulfonated phenolic formaldehyde (SPF) is shown in Figure 4.

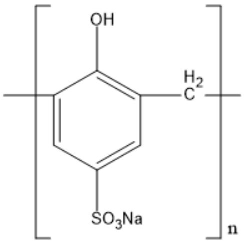


Figure 4. Chemical structure of sulfonated phenolic formaldehyde (SPF)

The degree of sulfonation (DS) is a decisive parameter controlling the balance between solubility and tanning power: high DS improves water solubility but may reduce tanning strength, while low DS enhances interactions with collagen fibers [11,5,9,12].

The performance of phenolic syntans is therefore a combination of polymer structure and sulfonation level. Controlling these factors allows tailoring of syntan properties for specific leather applications, ensuring optimal mechanical and physical characteristics. A systematic understanding of the interplay between polymerization and sulfonation is essential for producing syntans with consistent quality and performance [6,7,10].

Despite the extensive use of phenolic syntans, studies investigating the influence of reactant composition—particularly the phenol–formaldehyde molar ratio—on physicochemical properties remain limited. Critical properties such as pH, specific gravity, viscosity, and degree of sulfonation have not been comprehensively correlated with synthesis conditions, especially for locally produced syntans [9,5]. Addressing this gap is important for optimizing formulations and reducing dependence on imported chemicals in the leather industry. However, most previous studies have primarily focused on general synthesis or application performance without systematically correlating the phenol–formaldehyde molar ratio with key physicochemical parameters such as pH, viscosity, specific gravity, and degree of sulfonation in a unified framework. In addition, limited studies address the balance between polymerization and sulfonation mechanisms and their direct impact on syntan stability and phase behavior.

Therefore, the novelty of this study lies in providing a systematic evaluation of the structure–property relationship of phenolic syntans by simultaneously analyzing multiple physicochemical parameters under controlled molar ratio variations. This approach enables a clearer understanding of formulation optimization for locally produced syntans. Therefore, this study aims to evaluate the effect of phenol–formaldehyde molar ratio on the synthesis and physicochemical properties of phenolic synthetic tanning agents. The synthesized products were characterized using physicochemical analyses and Fourier Transform Infrared (FTIR) spectroscopy to confirm chemical structure and functional groups. By systematically investigating the relationship between reactant ratio, polymerization, and sulfonation, this research provides insights into tailoring syntans for improved leather processing performance [13,14,15,16,17,18,19,20].

Materials and Methods

Materials

Phenol (analytical grade) and formaldehyde solution (37 wt%) were used as the main precursors for syntan synthesis. Sulfuric acid (H_2SO_4) was employed as a catalyst in the polymerization step, while sodium bisulfite ($NaHSO_3$) was used as the sulfonating agent. Sodium hydroxide (NaOH) was utilized for pH adjustment. All chemicals were of analytical grade and used without further purification. Distilled water was used throughout the experiment.

Synthesis of Phenolic Syntan

Phenolic syntans were prepared through a two-step process consisting of condensation polymerization followed by sulfonation, based on a modified method from previous studies [7,3].

In the first step, phenol and formaldehyde were reacted under controlled conditions using various molar ratios (0:1, 0.5:1, 1:1, 1.5:1, 1:0.5, and 1:0). The reaction was conducted in a three-neck flask equipped with a mechanical stirrer, thermometer, and reflux condenser. The mixture was heated to 80–90 °C under acidic conditions, using sulfuric acid as a catalyst. The reaction proceeded for a predetermined period until a homogeneous phenolic resin was obtained.

In the second step, sulfonation was carried out by gradually adding sodium bisulfite to the phenolic resin while maintaining the temperature at 70–80 °C. The reaction continued until the target degree of sulfonation was achieved, producing a water-soluble phenolic syntan. The final product was cooled to room temperature and stored in sealed containers for subsequent physicochemical and spectroscopic analyses. The reaction time for the condensation step was maintained for approximately 60–90 minutes, while the sulfonation process was conducted for 60 minutes under continuous stirring at 300 rpm. The pH during synthesis was monitored and maintained in the acidic range (pH 2–3) using sulfuric acid. All experiments were conducted at least in duplicate to ensure consistency of observed trends. All experiments were conducted at least in duplicate to ensure reproducibility. The reaction temperature was maintained at 70–80 °C with continuous stirring at 300 rpm, and the pH was controlled in the range of 2–3 during synthesis.

Experimental Design

The study was conducted by varying the molar ratio of phenol to formaldehyde while keeping other synthesis parameters constant. Each formulation was coded accordingly (e.g., S1–S6). The variation in molar ratio was intended to investigate its effect on the physicochemical properties of the resulting syntan.

Physicochemical Characterization

The synthesized phenolic syntans were characterized using standard physicochemical methods. The pH of the syntan solutions was measured at room temperature using a calibrated digital pH meter. Specific gravity was determined with a pycnometer under ambient conditions, while viscosity was assessed using a rotational viscometer at controlled temperature. Additionally, the degree of sulfonation (DS) was quantified by titration to determine the content of sulfonate groups, following established procedures [11].

Fourier Transform Infrared (FTIR) Analysis

Fourier Transform Infrared (FTIR) spectroscopy was conducted to identify the functional groups present in the synthesized phenolic syntans. Spectra were recorded over the range of 4000–400 cm^{-1} using an FTIR spectrometer. The presence of characteristic absorption bands corresponding to aromatic rings, hydroxyl groups, and sulfonate ($-SO_3H$) groups was used to confirm the successful synthesis and sulfonation of the phenolic syntans [6].

Data Reliability

Since the measurements were conducted without full statistical replication, each test was repeated until stable and consistent values were obtained. Therefore, the results are presented based on comparative trends rather than statistical significance. This approach is considered acceptable for preliminary material characterization studies.

All measurements were conducted in repeated trials (at least duplicate measurements) until consistent values were obtained. Although full statistical analysis was not performed, the reproducibility of trends was ensured through controlled experimental conditions. The results are therefore presented as comparative trends suitable for preliminary material characterization.

Results and Discussions

For consistency, all values in this study are expressed using standard units: pH (–), specific gravity (–), and viscosity (cP).

Characteristics of Synthesized Syntans

The synthesized phenol–formaldehyde syntans exhibited distinct physical characteristics depending on the molar ratio of phenol to formaldehyde, as shown in Figure 5. Since the measurements were not performed under full statistical replication, the results are interpreted based on comparative trends. However, repeated measurements were conducted to ensure consistency and reliability of the observed data.

(a) (b)

Figure 5. Visual characteristics of synthesized phenol–formaldehyde syntans at varying molar ratios, showing the effect of phenol and formaldehyde composition on color and homogeneity.

All products were obtained in liquid form, indicating that the polymerization process did not lead to excessive crosslinking or gel formation. However, noticeable variations in color and clarity were observed. The absence of phenol resulted in a transparent solution, while increasing phenol concentration led to a gradual transition toward a pale yellow appearance. This behavior can be attributed to the formation of phenolic oligomers during condensation reactions. Higher phenol content promotes the formation of conjugated aromatic structures, which are known to absorb light in the visible region, thereby increasing color intensity. In contrast, variation in formaldehyde concentration at constant phenol levels showed minimal visual differences, indicating that phenol plays a more dominant role in determining chromophoric properties.

Effect of Reactant Ratio on pH and Degree of Sulfonation

Variation of Phenol Concentration

The effect of phenol concentration on pH and degree of sulfonation (DS) is presented in Figure 6.

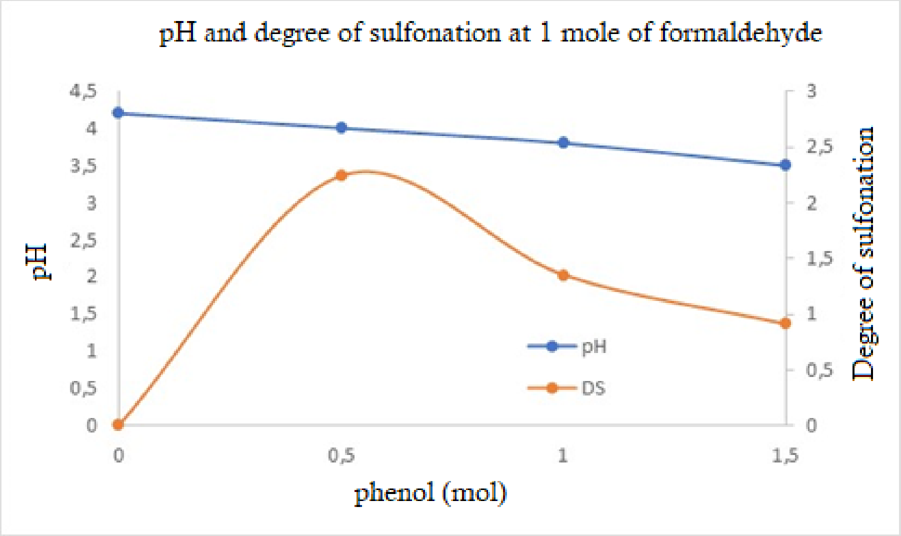


Figure 6. Effect of phenol concentration on degree of sulfonation (DS), showing an inverse relationship due to increased polymerization.

An increase in phenol concentration resulted in a systematic decrease in pH, indicating the increasing contribution of acidic functional groups in the system. This is consistent with the intrinsic weak acidity of phenol and the formation of phenolic hydroxyl groups during polymerization. The presence of these groups enhances proton donation, thereby lowering the overall pH.

Interestingly, the DS value decreased with increasing phenol concentration. This trend suggests that higher phenol content promotes extensive condensation reactions, which consume reactive sites (ortho and para positions) on the aromatic ring. As a result, fewer sites remain available for sulfonation, leading to lower incorporation of sulfonate groups. From an application perspective, this implies that excessive phenol may reduce the hydrophilicity of the syntan, as sulfonate groups are primarily responsible for water solubility and dispersibility in tanning systems.

Variation of Formaldehyde Concentration

The influence of formaldehyde concentration on pH and DS is shown in Figure 7.

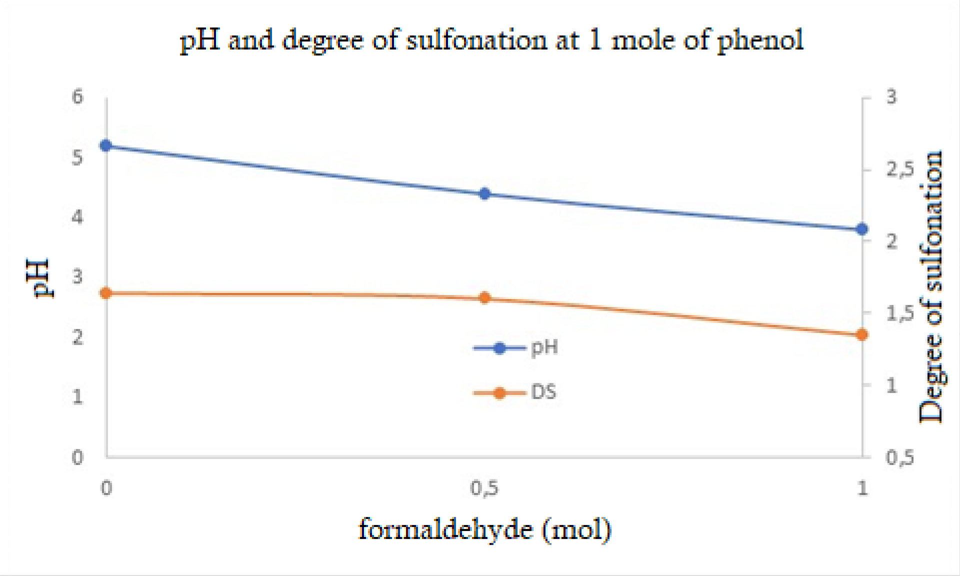


Figure 7. Effect of formaldehyde concentration on pH and degree of sulfonation (DS) of synthesized syntans at constant phenol concentration (1 mol).

Similar to phenol variation, increasing formaldehyde concentration resulted in a decrease in pH. This can be explained by the formation of hydroxymethyl intermediates and the slightly acidic nature of formaldehyde solutions. The accumulation of these species contributes to the overall acidity of the system.

In terms of sulfonation, increasing formaldehyde concentration led to a decrease in the degree of sulfonation (DS). Mechanistically, formaldehyde reacts with phenol to form methylol groups, which subsequently undergo condensation to form methylene bridges. When this reaction occurs extensively, the ortho and para positions of the aromatic ring become occupied, thereby limiting the accessibility of these positions for sulfonation.

Conversely, at lower formaldehyde concentrations, a larger fraction of reactive sites remains available, facilitating the incorporation of sulfonate groups and resulting in higher DS values. This indicates a competitive relationship between polymerization and sulfonation reactions, where excessive condensation reduces functional group availability. These findings are consistent with previous studies reported [11], which demonstrated that increasing crosslinking density reduces the availability of reactive sites for sulfonation. Similar behavior has also been observed in phenol–formaldehyde-based syntans, where the balance between condensation and sulfonation reactions plays a critical role in determining physicochemical properties [3,16].

However, compared to previous works, this study provides a more integrated analysis by simultaneously correlating polymerization behavior with phase stability and physicochemical properties. This highlights a clearer structure–property relationship of phenolic syntans, particularly the trade-off between polymer growth and functional group availability.

Such insights are important for optimizing syntan formulations, especially in balancing solubility, reactivity, and application performance. This aspect has not been extensively discussed in earlier studies, indicating the novelty of the present work.

Specific Gravity and Viscosity Behavior

The relationship between reactant composition and both specific gravity (SG) and viscosity is illustrated in Figures 8 and 9.

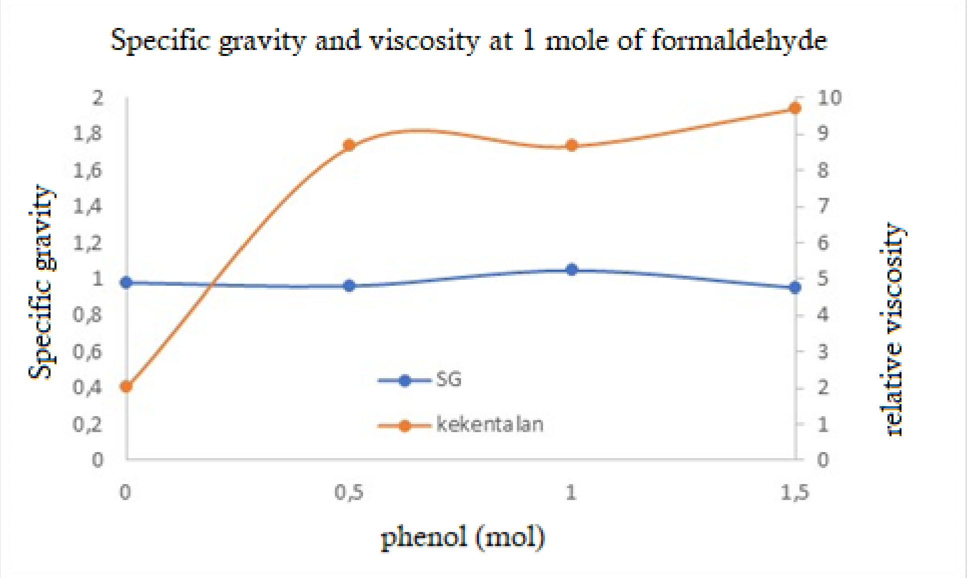


Figure 8. Effect of phenol concentration on specific gravity (SG) and viscosity of synthesized syntans at constant formaldehyde concentration (1 mol).

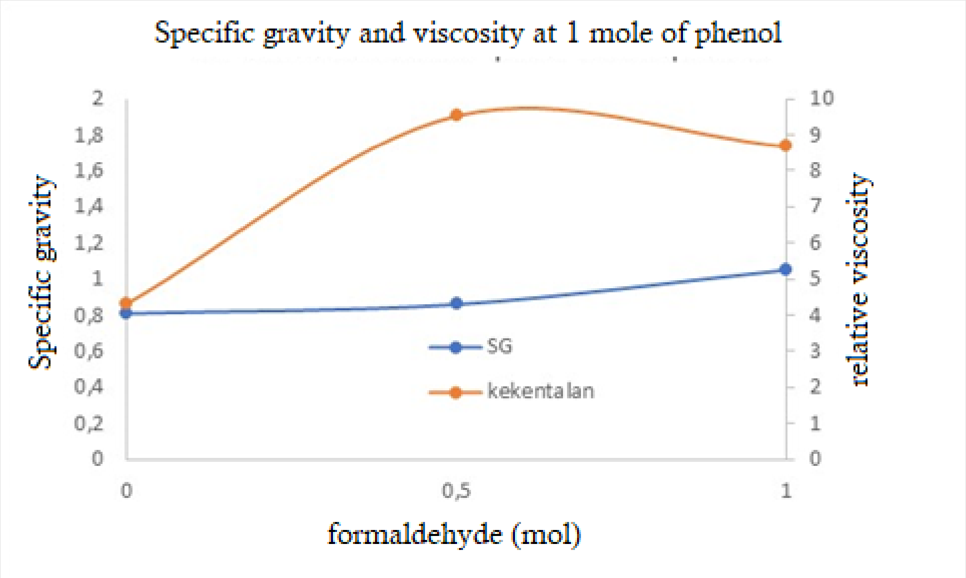


Figure 9. Effect of formaldehyde concentration on specific gravity (SG) and viscosity of synthesized syntans at constant phenol concentration (1 mol).

Both SG and viscosity increased with increasing phenol and formaldehyde concentrations, indicating the formation of higher molecular weight polymer chains and a more compact molecular structure. An increase in SG reflects a higher mass-to-volume ratio associated with greater polymer content, while the increase in viscosity suggests stronger intermolecular interactions and reduced molecular mobility. These trends are consistent with the behavior of phenol–formaldehyde resins, where increased condensation reactions lead to denser and more viscous polymer systems.

These findings confirm that higher reactant concentrations enhance the extent of polymerization. The consistent trends observed in both SG and viscosity further support that polymer growth is the dominant factor governing the physicochemical properties of the syntan. Similar observations have been reported in phenolic resin systems, where polymer network formation significantly influences rheological behavior and material density [10].

From an industrial perspective, viscosity is a critical parameter, as excessively high viscosity may hinder the penetration of syntans into leather fibers during application. Moreover, the balance between polymerization and functional group availability is essential, as excessive crosslinking may reduce the accessibility of sulfonic groups, which are responsible for solubility and dispersion in aqueous systems [11].

Nevertheless, the obtained SG and viscosity values fall within the typical range reported for commercial syntans, indicating that the synthesized products possess comparable physicochemical characteristics and potential applicability in leather processing. This is in line with previous studies on sulfonated phenolic systems, where structural modification through controlled sulfonation and condensation governs both physicochemical properties and application performance [12].

Compared to previous studies, this work provides a more integrated interpretation by simultaneously correlating viscosity, specific gravity, and sulfonation degree with reactant composition. This highlights a clearer structure–property relationship, particularly the trade-off between polymer growth and functional group availability, which has not been extensively discussed in earlier reports.

Phase Behavior of Syntans

The phase distribution of the synthesized syntans is summarized in Tables 1 and 2.

Table 1. Phase behavior and visual characteristics of phenolic syntans at varying phenol-to-formaldehyde molar ratios (formaldehyde fixed at 1 mol)

Sample	Phenol : Formaldehyde Ratio	Phase Condition	Description
A	0 : 1	Single phase	Clear and homogeneous liquid
B	0.5 : 1	Two phases	Slight phase separation with light color difference
C	1 : 1	Single phase	Homogeneous and stable liquid
D	1.5 : 1	Two phases	Visible phase separation with darker upper layer

Table 2. Phase distribution and stability of syntans at constant phenol concentration (1 mol) with varying formaldehyde ratios

Syntan Sample (Phenol:Formaldehyde Ratio)	Parameter	(1:0)	(1:0.5)	(1:1)
Sample Code		E	F	C
Phase Distribution		2 phases	2 phases	1 phase
Phase Color		Clear / Turbid	Clear / Yellowish	Clear

Although all syntans were obtained in liquid form, several formulations exhibited phase separation. This indicates the presence of components with different polarity or molecular weight distributions.

Phase separation is likely caused by incomplete compatibility between highly condensed polymer fractions and more hydrophilic sulfonated components. Over time, these differences lead to segregation into distinct layers.

Notably, syntans with a balanced molar ratio (P:F = 1:1) showed a more homogeneous phase, suggesting optimal interaction between condensation and sulfonation processes. This balance appears to be critical in achieving stable and uniform syntan products.

This observation further emphasizes the novelty of this study in linking molar ratio not only to chemical properties but also to phase stability, which is critical for practical application. Such insights are important for industrial-scale formulation where homogeneity directly affects processing performance.

FTIR Analysis

The FTIR spectra (Figures 10–12) confirm the successful formation of sulfonated phenol–formaldehyde polymer structures through the identification of characteristic functional groups.

A broad absorption band observed at 3300–3400 cm^{-1} corresponds to O–H stretching vibrations, indicating the presence of phenolic hydroxyl groups and hydrogen bonding interactions within the polymer matrix. This feature is typical for phenolic resins due to their highly functionalized aromatic structure.

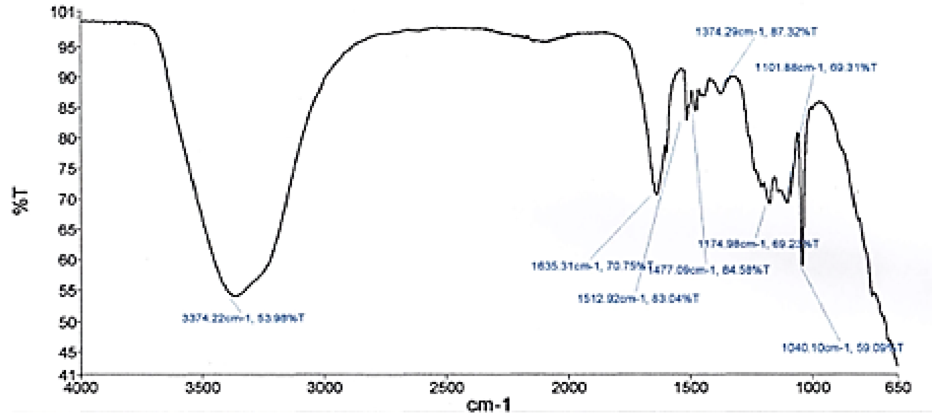


Figure 10. FTIR Spectrum of Phenolic Syntan at a Phenol-to-Formaldehyde Ratio of 0.5:1

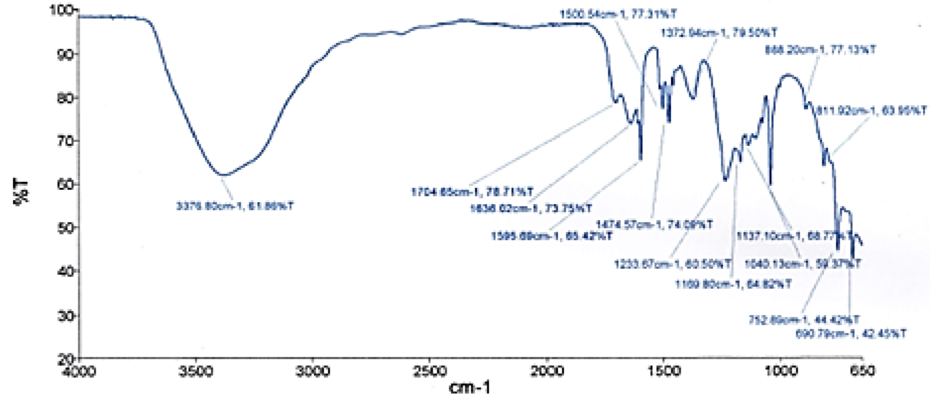


Figure 11. FTIR Spectrum of Phenolic Syntan at a Phenol-to-Formaldehyde Ratio of 1:1

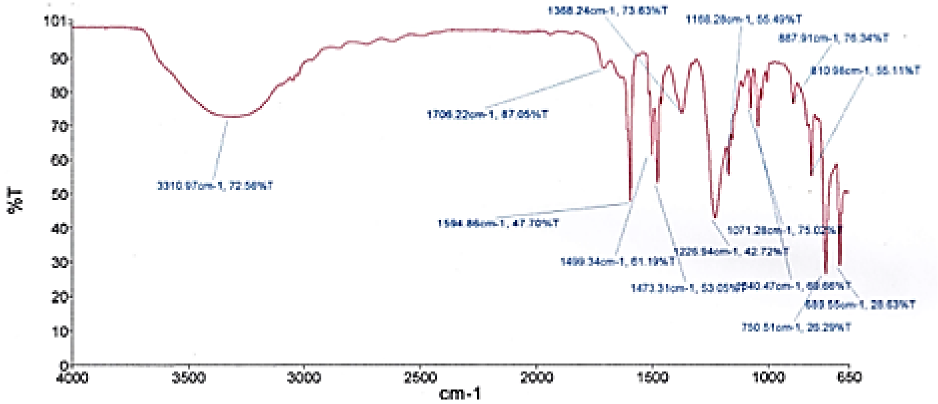


Figure 12. FTIR Spectrum of Phenolic Syntan at a Phenol-to-Formaldehyde Ratio of 1:0.5

The peaks in the region of 1500–1600 cm^{-1} are assigned to aromatic C=C stretching vibrations, confirming the formation of substituted benzene rings as the backbone of the polymer. In addition, a band around 1450–1470 cm^{-1} is attributed to methylene bridge (–CH_2–) linkages, which are key indicators of successful polymerization and crosslinking within phenol–formaldehyde systems.

Absorption bands in the range of 1000–1200 cm^{-1} correspond to C–O and C–O–C stretching vibrations, indicating the formation of ether linkages during condensation reactions. Furthermore, peaks around 1030–1080 cm^{-1} suggest the presence of sulfonate (–SO_3H) groups, confirming successful sulfonation and enhanced hydrophilicity of the syntan.

Overall, the FTIR results validate the formation of a crosslinked phenolic polymer structure with incorporated sulfonate groups. These structural features are directly associated with improved solubility, reactivity, and interaction with collagen fibers, which are essential for leather processing applications.

Conclusion

This study demonstrates that the phenol–formaldehyde molar ratio plays a critical role in determining the physicochemical properties of phenolic syntans, particularly pH, degree of sulfonation, viscosity, specific gravity, and phase stability. The results reveal a clear trade-off between polymerization and sulfonation, where increased reactant concentration enhances polymer formation but reduces the availability of reactive sites for sulfonation.

The optimal molar ratio (1:1) was identified as producing the most stable and homogeneous system, indicating a balanced interaction between condensation and sulfonation processes. This finding highlights the importance of formulation control in achieving desirable syntan characteristics.

The main contribution of this work lies in establishing a systematic structure–property relationship of phenolic syntans based on reactant composition, which provides a scientific basis for optimizing syntan design. Practically, these results can support the development of more efficient and tailored syntans for leather processing applications.

Future work should focus on statistical validation and application testing on leather to further confirm the industrial relevance of the synthesized materials.

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