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Development of a casein-based matrix and mechanical properties of sustainable composites from cellulose and cellulose acetate: A preliminary study

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Abstract. The development of sustainable composite materials has gained increasing attention as industries seek eco-friendly alternatives to synthetic polymers. Casein, a protein derived from milk, represents a promising renewable resource for such applications due to significant waste of milk surplus. However, its broader use has been historically limited by the poor mechanical performance and water sensitivity. In this study a novel casein based sustainable composite has been developed by optimizing a casein-based matrix and reinforcing it by biodegradable fibers, specifically cellulose and cellulose acetate. Flexural and shear strength tests outlined the enhancement of the fiber-matrix adhesion and the mechanical performance, making these composites suitable for various applications, including packaging and construction. Therefore, the novel realized composite is a valuable material that enables the reuse of dairy surplus milk and contributes to the reduction of the environmental footprint associated with composite production.

Introduction

Casein, a phosphoprotein derived from milk [1,2], has a long history of use as a natural adhesive due to its remarkable bonding properties. Its applications date back to ancient Egypt [3], where it was employed in woodworking, and extend through the Middle Ages, contributing to the production of art and musical instruments [1,4]. During the 20th century, casein adhesives played a key role in industries such as plywood manufacturing for early aircraft [5–7]. Despite its historical importance, casein's industrial applications today are limited, representing only a minor fraction of global milk production. This is especially noticeable given the significant quantities of surplus milk annually wasted [8], which evidences the potential for reusing casein into high-value products.

The increasing demand for sustainable materials has attracted renewed interest in natural alternatives like casein. Unlike synthetic adhesives and matrices, which are often derived from fossil fuels and release harmful substances such as volatile organic compounds (VOCs) during their lifecycle, casein is renewable, biodegradable, and non-toxic [9]. These attributes make it a potential candidate for replacing petroleum-based materials in various industries. However, traditional casein formulations [5] present drawbacks, including low mechanical strength and high-water sensitivity, which have limited their use in structural and durable applications.

To address these limitations, this study investigates the development of a novel casein-based matrix for composite materials. Building upon traditional casein adhesives, the matrix formulation was enhanced to improve its mechanical properties and adaptability. Reinforcement was achieved by incorporating cellulose and cellulose acetate fibers, both recognized for their biodegradability, mechanical strength, and compatibility with natural matrices [10]. The developed fiber-reinforced system takes advantage from the synergistic properties of casein and biodegradable fibers to produce composite materials with superior performance and reduced environmental impact.

The developed composite materials were subjected to mechanical testing, including flexural and shear strength evaluations, in order to assess their structural integrity and fiber-matrix adhesion. These tests are fundamental for determining the suitability of the composites for applications in industries such as construction, packaging, and automotive manufacturing, where mechanical performance and sustainability are key considerations. The experimental mechanical results outlined the potential of cellulose reinforced casein-based matrices as novel sustainable composites alternative to synthetic composites, not only to use renewable resources, but also to reduce dependence on non-renewable inputs, supporting the transition to a more circular economy.

Materials and Methods

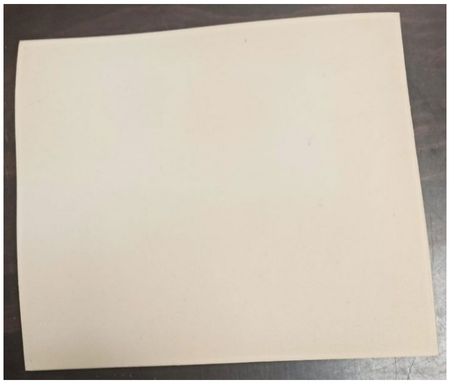
Casein. The lactic casein used in this study was sourced from AN.T.A.RES Ltd. (located in Italy), produced by acid precipitation from surplus waste milk and subsequently dried. Its key properties include a powdery solid appearance, creamy-white colour, and characteristic smell. It is low soluble in water and insoluble in alcohol and ether, while it dissolves in alkaline solutions. Its composition includes a protein content of up to 90%, with minimal fat (1.5%) and ash (2.5%) content. It is primarily used in producing caseinates like ammonium caseinate for paints and calcium caseinate, a durable adhesive used in natural composite matrices.

Lime putty. Slaked lime from the Stilema line produced by Sestriere Vernici (located in Italy) was used. It is a ready-to-use mixture containing 50.4 % w/w CaO, 17.4 % w/w MgO, H2O combined by 23.4% w/w other oxides. It has a density of 1.6 g/cm3, is shiny and glossy in colour and has excellent anti-mould, antibacterial and weathering properties.

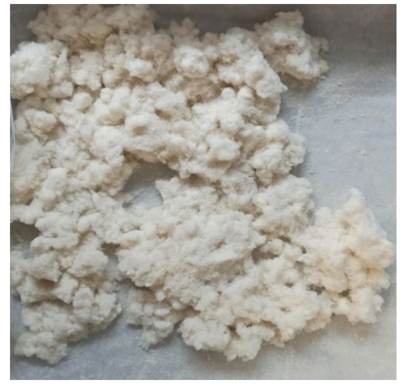
Fibers. To produce the cellulose flakes needed for the casein-based composites, a pure cellulose panel measuring 50x50 mm (Figure 1) was used. The material was cut into varying fragments to obtain the required micro-cellulose. These fragments were then subjected to centrifugation in a blender with water ensuring full saturation of the fragments. The mixture was blended for several minutes to achieve homogeneous, well-mixed microfibers.

Then, the fibers underwent a complete drying process to remove residual moisture. They were left to air-dry at room temperature for 12 hours before being placed in an oven set at 50°C for 8 hours to finish drying.

The result of the micro-cellulose production process is shown in Figure 1 , where the dried flakes are visible, representing the essential fibrous component for the composite matrix, which will be based on casein glue.



a)



b)

Figure 1 – Micro-cellulose production process: (a) Cellulose panel (50x50 mm) used to obtain the required micro-cellulose flakes. (b) Dried micro-cellulose flakes, the essential fibrous component for the casein-based composite

The virgin cellulose acetate fibers were sourced from unused cigarette filters commercially available (Rizla+). These filters were placed inside a mixer to break them down into microfibers, which were then processed further for use in the composite materials.

Casein-based matrix. To prepare casein-based adhesives, casein is treated with alkaline substances such as calcium hydroxide (lime putty) after being diluted in water, allowing it to dissolve and form a gel-like consistency. Traditionally, casein, water and lime putty have been used in various ratios to realize these adhesives, which densify quickly as strong chemical bonds form between the ingredients, resulting in a robust network structure [11].

The traditional formulation of casein-based adhesive can present limitations: if excessively liquid, it loses stability and becomes challenging to handle, while if too viscous, it dries out and does not penetrate the substrate adequately. In this study, the casein-based matrix was derived from the traditional casein adhesive formulation [5], with the specific quantities shown in Table 1. Two different solutions were prepared to improve the matrix's performance. The first solution consists of 30 grams of casein dissolved in 90 grams of distilled water, prepared at least 24 hours in advance to allow proper swelling of the casein and promote better interaction with water. The mixture is periodically stirred to ensure uniformity. The second solution includes 45 grams of lime putty mixed with 30 grams of distilled water, which prevents lump formation and ensures a homogeneous final matrix. By keeping separate the two components, premature reactions are avoided, allowing for better control during mixing.

Table 1 – Formulation of the casein-based matrix

	Elements	**Quantity (grams)**	**Percentage (% of total weight)**
Solution 1	Casein	30	15.38
	Water	90	46.15
Solution 2	Lime putty	45	23.08
	Water	30	15.38
Total Water		120	61.54

Sonication was applied both to the casein solution and the final matrix with the aim to enhance the matrix homogeneity by disrupting the casein micelles, which made the adhesive denser and more uniform. It also reduced air entrapment, evident by foam forming at the air-adhesive interface. Additionally, sonication enhanced diffusion of calcium hydroxide, providing a smoother, lump-free paste including casein micelles, arranged into a stable network-like structure, as confirmed through optical microscopy.

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Composite manufacturing. The composite was realized by using micro-cellulose flakes as reinforcing fibers, accounting for 50% by weight of the total matrix. Two types of composites were produced depending on the used fibers: C_{CEX}, made with virgin cellulose, and C_{ACX}, made with virgin cellulose acetate. In the composite codes, 'C' stands for composite, 'CE' for cellulose, 'AC' for cellulose acetate, and 'X' represents the sample number tested.

The micro-cellulose flakes were carefully blended with the casein matrix to create a uniform mixture, ensuring optimal fiber impregnation. Achieving uniformity in the mixture is critical for a homogeneous distribution of matrix and fibers within the composite, which directly influences the material's final quality.

The next step involved compression moulding. The homogeneous mass was placed into a 100 x 150 mm mould (Figure 2) which was accurately cleaned and coated with a thin layer of wax to prevent adhesion. A mechanical press was then used to fix the composite's thickness and optimize material distribution across the mould surface. Applying the correct compression force, kept at 1 bar, was critical to avoid excessive pressure, which could cause unwanted material overflow, and to ensure the production of a high-quality composite.

Figure 2 – 100 × 150 mm mould containing the composite material, prepared for the compression moulding process

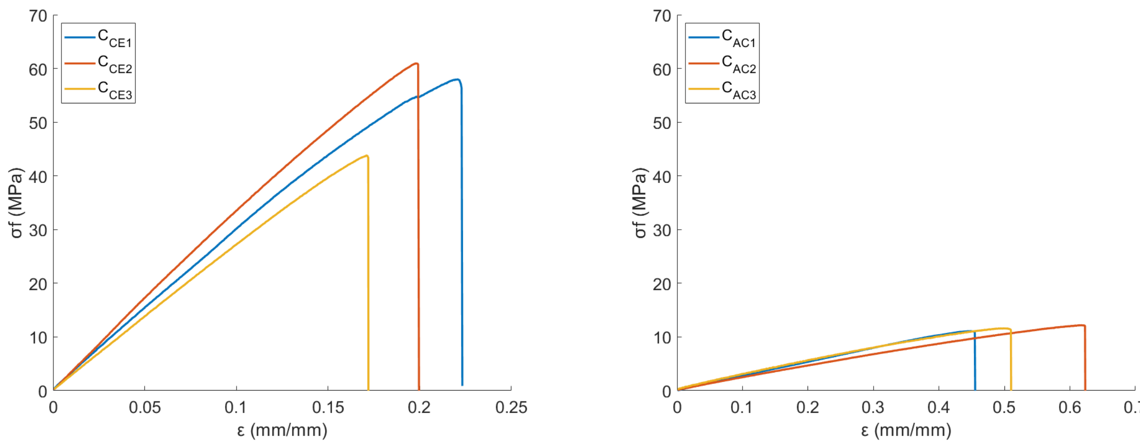
Once compressed, the mould was placed in an oven at 50°C for 24 hours to facilitate complete drying of the material. To further remove residual moisture and prevent warping, a clamping frame was used. Initially, a solid, non-perforated frame was tested, but it yielded suboptimal results, negatively affecting the composite's mechanical properties. On the other hand, switching to a perforated frame significantly improved products, as the perforations allowed better airflow and more effective moisture removal. After ensuring the composite was fully cured and moisture-free, mechanical tests were performed to assess its structural performance and suitability for various applications. The visual inspection of the realised composites evidenced a more pronounced non uniform shrinkage of samples made of virgin cellulose fibers.

Results and discussion

Flexural tests. To assess the flexural properties of composites made from a casein-based matrix, cellulose acetate, and cellulose, both strength and flexibility were measured. Testing was performed by using a flexural testing machine (MTS Alliance RT/50) with a 1kN load cell, in accordance with the three-point bending configuration outlined in ASTM D790 standards. The composite material was cut into standardized test specimens per ASTM D790 guidelines, ensuring all samples were properly conditioned and free from visible defects. During testing, each specimen was supported at two points and subjected to a load at the midpoint, with a span length set at 32 times the specimen's thickness. Figure 3 illustrates the stress-strain (σ-ε) curves for both cellulose and cellulose acetate, while Table 2 reports a summary of the obtained results.

Table 2 – Summary of flexural test results for cellulose and acetate cellulose composite

Id Composite	Code	Maximum Load (N)	Flexural Strength (MPa)	Flexural Modulus (MPa)
Cellulose Composite	C_{CEX}	23.81	53.38±8.76	5985.72±551.67
Acetate Cellulose Composite	C_{ACX}	10.90	11.17±0.37	506.27±56.44



a) b)

Figure 3 – Stress-Strain (σ-ε) curve for the cellulose (a) and acetate cellulose (b) composite.

Shear tests. Shear properties of composites made with a casein-based matrix and cellulose acetate, or cellulose were evaluated using a shear testing machine (MTS Alliance RT/50), following the ASTM D2344 standards. Specimens were prepared with standardized dimensions and conditioned. The shear test adopted a short-beam shear fixture, with two supports positioned at the ends of the specimen and a loading nose applied centrally between them. In accordance with ASTM D2344, the support span was set to approximately four times the specimen's thickness. The specimen was placed horizontally on the supports, and a vertical load was applied at the midpoint by the loading nose, generating shear stress within the specimen. The results of the shear test, including key metrics such as maximum shear load and shear strength for both cellulose and cellulose acetate composites, are summarized in Table 3.

Table 3 – Summary of shear test results for acetate cellulose and cellulose composites

Id Composite	Maximum shear load (N)	τ_{max} (MPa)
Cellulose Composite	86.65	6.79±0.59
Acetate Cellulose Composite	48.275	2.78±0.55

Discussion. Analysis of composites made from different types of cellulose fibers reveals a significant shrinkage difference during the solidification of the casein matrix. This uneven shrinkage leads to considerable variations of the panel thickness, which in turn affects the consistency of test results. Thus, the most reliable parameters for comparing the composite mechanical performance with different fibers are those related to the flexural modulus and short-beam shear strength. The experimental test results show better mechanical performance for the composites based on virgin cellulose fibers. Specifically, for the flexural modulus, composites with virgin cellulose fibers achieved a maximum value exceeding 6.0 GPa, while panels made

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from commercial cellulose acetate fibers (from cigarette filters) displayed much lower values, around 500 MPa. This difference can depend on two main factors, such as the different chemical structure of cellulose and cellulose acetate and the composition of commercial cellulose acetate. In fact, cellulose acetate can be obtained through the esterification of cellulose with acetic acid and is characterized by the substitution of cellulose hydroxyl groups by acetyl groups. Thus, its solubility and mechanical properties are affected by the degree of substitution of hydroxyl groups, that, in the case of cellulose, enable the formation of hydrogen bonds and of a more rigid structure with higher glass transition temperature [12]. In addition, the commercial cellulose acetate includes some plasticizers, as triacetin and polyethylene glycol, which interact with the casein matrix and increase its flexibility by reducing its stiffness and thereby weakening the composite's overall mechanical performance. Additionally, plasticizers likely reduce the fiber-matrix adhesion, decreasing the efficiency of load transfer under stress.

Shear tests further support these findings, showing an average shear strength of 6 MPa for composites with virgin cellulose fibers, compared to significantly lower values (2–3 MPa) for those made with cellulose acetate fibers.

Conclusion

This study highlights the potential of casein-based matrices reinforced with virgin cellulose and cellulose acetate fibers as sustainable composite materials. The experimental results indicate that the fiber type significantly affects the mechanical performance of the composites. Composites with virgin cellulose fibers exhibited superior mechanical properties, especially flexural modulus and shear strength, demonstrating values exceeding 6.0 GPa and 6 MPa, respectively. In contrast, composites made with cellulose acetate fibers, derived from cigarette filters, showed markedly lower performance, induced by the intrinsic chemical structure and the interaction between the plasticizers in the acetate and the casein matrix.

On the basis of these findings, in the future the entire manufacturing process of the composite will be more examined and optimized by exploring the formulation of the casein-based matrix, its curing process and advanced technologies. These innovations aim to further improve the mechanical properties and stability of the composites, making them more competitive with traditional synthetic materials.

From a sustainability perspective, this study contributes to the development of eco-friendly materials that not only utilize renewable resources like cellulose and casein but also promote the circular economy by reusing waste products, such as surplus milk. By reducing reliance on fossil-based materials, these composites offer a pathway to lower carbon emissions and minimize environmental impact, aligning with global efforts to achieve sustainable production and consumption. Future advancements in scaling up these materials could lead to broader applications in packaging, construction, and beyond, supporting industries in their transition to greener alternatives.

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