Journal of
Composites Science

Article

A Preliminary Investigation on the Thermal Behavior of Polysaccharides-Modified Casein

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Abstract: The effective use of natural casein-based adhesives requires the reduction of shrinkage phenomena associated with the evaporation of water, which is largely used for preparation. After the procedure optimization of a casein natural glue by aid of an alkaline solution, it was modified by the addition of two different sugars with long and short chains—chitosan and dextrose, respectively—at different weight concentration levels to absorb and retain water. The thermal decomposition and degradation kinetics of prepared sugar-based casein glues have been analyzed by performing thermogravimetric TGA characterization at different heating rates. Experimental results and the evaluation of thermal degradation activation energy by Kissinger analysis evidenced that the chitosan and dextrose could be efficient and sustainable additives to control and mitigate the degradation mechanisms of casein glues. Further, vertical flammability tests (UL 94 standards) on the sugar-modified casein materials with the highest sugar content confirmed the positive effect of chitosan and dextrose addition under flame exposure too.

Keywords: casein; chitosan; dextrose; degradation

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Academic Editors: Shreya Vemuganti and Jeffery S. Volz

Received: 14 May 2025
Revised: 13 June 2025
Accepted: 17 June 2025
Published: 19 June 2025

Citation: Ricciardi, M.R.; Russo, M.; Antonucci, V.; Affatato, L.; Langella, A. A Preliminary Investigation on the Thermal Behavior of Polysaccharides-Modified Casein. *J. Compos. Sci.* **2025**, *9*, 314. https://doi.org/10.3390/jcs9060314

1. Introduction

In recent years, the study and the production of healthier, safer, and more environmentally friendly materials throughout their entire life cycle has become a priority for researchers, designers, and producers, due to the need to reduce pollution, toxicity, and waste. Therefore, scientific interest is particularly focused on the development of new bio-based materials with performance and physical–chemical properties similar to those of commonly used synthetic materials. In particular, bio-based adhesives and resins, as replacement for synthetic ones, are continuously explored in order to mainly toxicity and disposal, related to the emission of formaldehyde and volatile organic compounds (VOCs) [1]. Biopolymers are polymeric materials made from bio-based and/or biodegradable raw materials, and they have intrinsic properties such as biodegradability, biocompatibility, non-toxicity, and sustainability. In general, biopolymers can be classified into three main groups: nucleic acids and nucleotides; proteins and amino acids; and carbohydrates [2].

Casein is an interesting natural protein, and a valid alternative to synthetic adhesives. It is a biopolymer derived from milk proteins and, when properly modified, can become a sustainable adhesive. Its use as glue has been known since Ancient Egypt due to better coloration and significant water resistance compared to other natural or animal adhesives [3–5]. Casein has been extensively studied and is applied for many uses in cosmetics, food, drug industries, packaging [6], and structural applications, such as plywood and laminates [7–10], as well as flame-retardant materials for textiles [11]. However, despite its interesting properties and significant annual milk waste (18% of production), commercial casein applications are still limited [6] and should be encouraged in order to reduce the milk surplus and valorize it as a natural resource [12].

Casein is the main protein of bovine milk, representing about 80% of the whole protein content [8]. The chemical structure is that of a block bio-copolymer, a phosphoprotein that has poor solubility in water but is very soluble with the addition of a base [13]. Due to the hydrogen bonds, the casein molecule has a spiral shape where the polar amino acids groups are available for reactions just after alkaline treatment. The casein proteins are colloidal particles, referred to as casein micelles, with diameters ranging between 9 and 150 nm. Casein-based adhesives can be produced thanks to the solubility of casein in alkaline solutions [14–16], which enables the unrolling of the micelles and makes available the reactive polar groups useful for bonding. The selection of the proper alkaline agent is fundamental for the expected properties of casein glue. For example, calcium hydroxide provides adhesives with good water resistance, but low shelf life. On the other hand, sodium hydroxide enables the formation of adhesives with extended durability, but low water resistance [17]. The formation of caseinates, such as calcium caseinate, also known as “casein glue”, provides the preparation of strong, resistant, and insoluble adhesives. However, the effective use of these natural adhesives requires a reduction of the overall volume loss that occurs during the drying phase due to the water evaporation and leads to undesired thermal shrinkage. The adoption of polysaccharides during casein glue preparation can slow down the evaporation process. In fact, thanks to the presence of amine and hydroxyl functional groups, polysaccharides are able to absorb and retain water, allowing for more gradual drying and consequently reducing shrinkage. Among polysaccharides, chitosan is emerging as one of the most promising candidates to formulate novel environmentally friendly bioadhesives [18–25] and to replace synthetic petrochemical adhesives. In fact, it has recently attracted the attention of many researchers [18–25] due to its characteristics, such as good mechanical properties, its insolubility at neutral pH, and its solubility in acidic conditions. It can be obtained by the deacetylation of chitin, is not toxic, and is biodegradable. In addition, thanks to its high crystallinity and extensive hydrogen-bonding capacity in the presence of numerous hydroxyl groups, it exhibits excellent oxygen barrier properties, cohesive strength to materials, and an intrinsic film-forming ability, making it a promising matrix for adhesive systems in the packaging industry. For example, Vrabič-Brodnjak [26] developed chitosan-based adhesives in combination with tannic acid and shellac, and reported an improvement of tensile strength up to 30% for the realized bioadhesive with respect to commercial and synthetic solutions.

In this work, a casein glue has been realized by using lime putty and optimizing the preparation procedure. The casein glue was then properly modified by the addition of chitosan and dextrose, two sugars with long and short chains, respectively, at different weight concentration levels, in order to reduce undesired shrinkage phenomena associated with the evaporation of the high water content. The thermal resistance and the flammability behavior of the sugar-modified casein glues has been investigated. In particular, the thermal decomposition and degradation kinetics have been analyzed by performing thermogravimetric TGA characterization at different heating rates (5, 10, 15, and 20 °C/min). Experimental results and the evaluation of thermal degradation activation energy by Kissinger analysis evidenced that the chitosan and dextrose could be efficient and sustainable additives to control and mitigate the degradation mechanisms of casein glue. Further, to assess the interaction and beneficial effect of sugar addition, FT-IR analysis and vertical flammability tests have been performed for the casein and the polysaccharides formulations with the highest content (50%*w*/*w*), demonstrating the enhancement of the casein flammability too.

2. Materials and Methods

2.1. Materials

The used casein is a bovine lactic from AN.T.A.RES srl (San Lazzaro di Savena (BO)–Italy) It is obtained from fresh milk through acid precipitation and drying. Casein is the main family of phosphoproteins present in the milk of mammals [2]. It consists of tightly coiled chains of secondary amino acids. Table 1 shows the main chemical and physical characteristics of the adopted casein.

Table 1. Chemical and physical characteristics taken from the data sheet of the used lactic casein.

Properties	Details
Appearance	Powdery solid
Color	Creamy-white
Odor	Characteristic
Solubility	Sparingly soluble in water, swelling in water. Insoluble in alcohol, ether. Soluble in solutions of ammonia, borax, caustic alkali, bicarbonates, carbonates, phosphates, other alkali salts.
Grain size	90 mesh
Moisture	12% max.
Composition (indicative)	Protein (dry): 90% max. Fat: 1.5% max. Ash: 2.5% max. Acidity: 1% max.

The chitosan (molecular weight in the range of 50,000 to 190,000 Dalton) and dextrose used as fillers in the production of developed natural composites are those produced by SIGMA-ALDRICH (Milan, Italy)

The lime putty from the Stilema line produced by Sestriere Vernici (Nichelino, Italy) is a ready-to-use mixture consisting of 50.4% CaO, 17.4% MgO, 23.2% H_2O, and the remaining portion of other oxides. It has a density of 1.6 g/cm^3, a bright and shiny appearance, and exhibits excellent anti-mold, antibacterial, and weather-resistant properties. Leaves, collected on the Campania coast, have been dried in a vacuum oven in two steps: at 100 °C for 2 h and at 80 °C for 22 h. Then, the material has been chopped by a grinder and milled in order to reduce the powder material into granules (by Retsch Mulino Ultra Centrifugal ZM 100-Haan Germany, Retsch, Haan, Germany). The morphology and fracture surface of the Posidonia powder and resins were studied by using Esem_Fei_Inspect_S, Electron microscope coupled with Oxford INCA PentaFETx3 EDX spectrometer, which is a Si(Li) detector, nitrogen cooled and equipped with an ultrathin window ATW2. The results were then processed by an INCA software energy (V7). In addition, the average PO particle size was estimated via a laser diffraction technique using Helos equipment (by Sympatec GmbH, Torre Boldone, Italy).

2.2. Preparation

The formulation of casein glue is as follows: 30 g of casein, 60 g of water, and 22.5 g of lime putty, with the addition of chitosan and dextrose from 10% to 50% relative to the weight.

The preparation of the glue involves the preliminary preparation of two separate solutions based on casein and lime putty, respectively. The first solution is realized by dissolving 30 g of casein in 60 g of distilled water, prepared at least 24 h in advance to allow the micelles separation and provide the proper equilibrium assembly of casein micelles. The mixture is periodically stirred to ensure uniformity. The second solution consists of 45 g of lime putty mixed with 30 g of distilled water, which helps to prevent swelling formation and ensures a smooth, consistent matrix. Table 2 shows the detailed quantities and concentrations of both solution formulations.

Table 2. Formulation of the casein-based matrix.

	Components	Mass (Grams)	Percentage (%)
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

The first solution is then modified by the addition of chitosan (CH) or dextrose (DX) to mitigate shrinkage during the drying phase, as the evaporation of water results in a decrease in overall volume. Starting from the base casein formulation (RB), several samples (CH10, CH20, CH30, CH40, CH50, DX10, DX20, DX30, DX40, and DX50) were prepared with different weight percentages of polysaccharide, specifically 10, 20, 30, 40, and 50% relative to the weight of casein. The solution is mechanically mixed until a homogeneous mixture is obtained and then sonicated in an ultrasonic bath at a frequency of 59 kHz for 10 min. Sonication promotes the dissolution of aggregates, such as casein micelles, overcoming the cohesive forces between protein molecules and realizing a solution with a network of protein material aggregates.

After sonication, the slaked lime is added, and the samples are cured at 60 °C for 24 h.

The weight and diameter percentage change before and after drying were evaluated in order to analyze the influence of polysaccharides on the material's extent of shrinkage due to the water evaporation. Figures 1 and 2 respectively show the weight loss and shrinkage percentage as a function of the sugar content within the casein matrix before and after oven curing for 12 h for each prepared material.

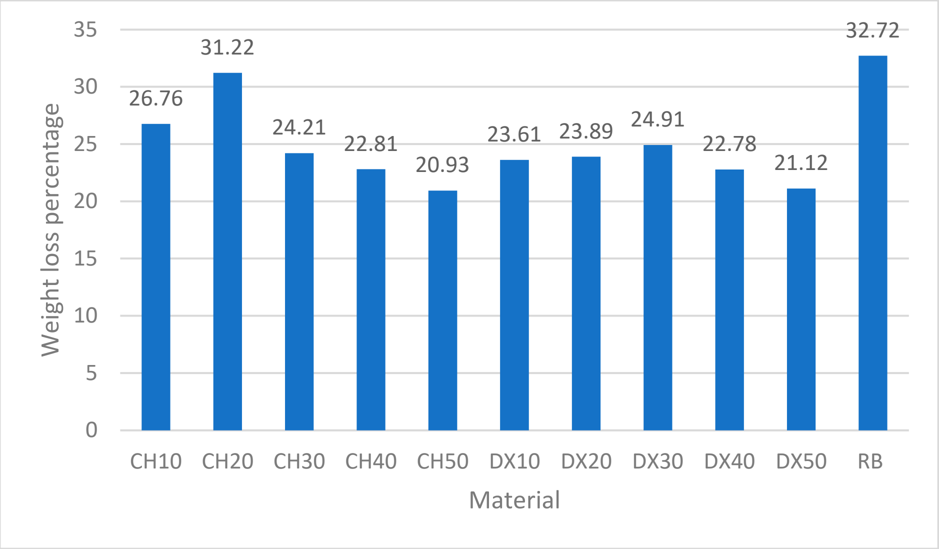

Figure 1. Weight loss percentage for each prepared material system.

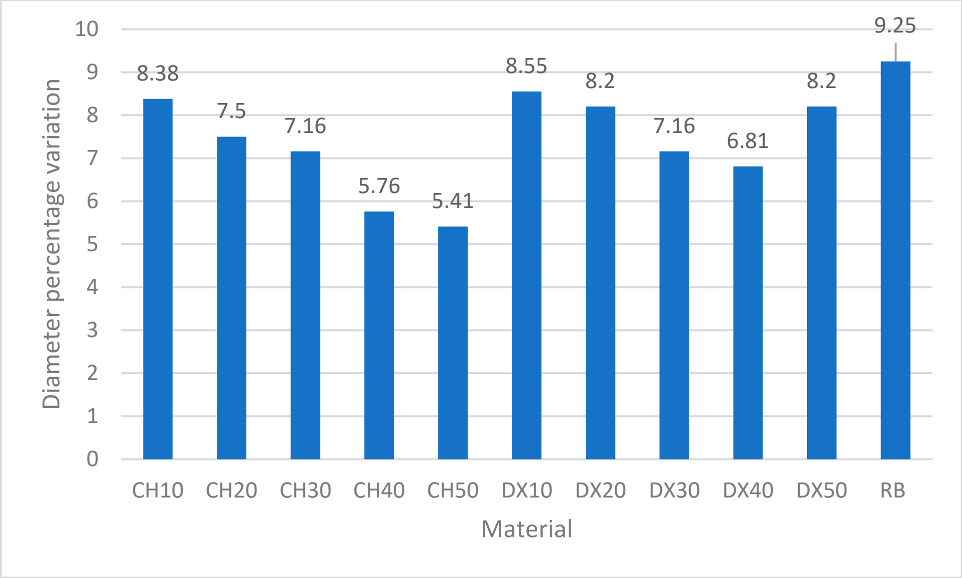

Figure 2. Percentage shrinkage for each prepared material system.

Both chitosan and dextrose have a positive effect on water retention. In particular, it is possible to notice that the material based on 50%w/w of chitosan exhibits the smallest weight and diameter percentage changes.

Consequently, after the drying process, the appearance of the samples was quite different, as shown in Figure 3, where the pictures of more significant materials are reported and the reduced shrinkage of saccharides-based casein materials is evident (Figure 3).

Figure 3. Post-oven drying samples.

2.3. Methods

Thermogravimetric analyses (TGA) were performed by using TGA system Q500 Ta Instruments under a nitrogen system, and by using four heating rates from ambient temperature to 100 °C: 5,10, 15, and 20 °C/min. Vertical flammability tests were carried out according to UL 94 standards [27] on the neat casein systems and modified casein systems CH50 and DX50 50%. To ensure reliability and significance of results, both tests were repeated 5 times for each type of sample.

Fourier transform infrared analysis was performed by Frontier MIR/Fir Spectrometer Perkin Elmer equipment (Springfield, Springfield, MO, USA) on the neat casein and on the modified casein systems with 50% w/w sugar percentage in order to investigate the interaction mechanism between the casein and both polysaccharides.

3. Results

3.1. Thermogravimetric Analysis: Experimental Results and Kissinger Methods

The effect of sugar addition on the thermal stability of the casein was investigated by thermogravimetric TGA tests that have been performed for all prepared formulations at different heating rates of 5, 10, 15, and 20 °C/min under nitrogen atmosphere. Figures 4 and 5 show the TGA curves and the degradation stages for casein at all heating rates. According to study [28], the thermal degradation proceeds into four stages. Table 3 shows the characteristic temperatures, weight residual, the maximum rate of degradation, and the corresponding temperature associated with each stage for the test at 10 °C/min.

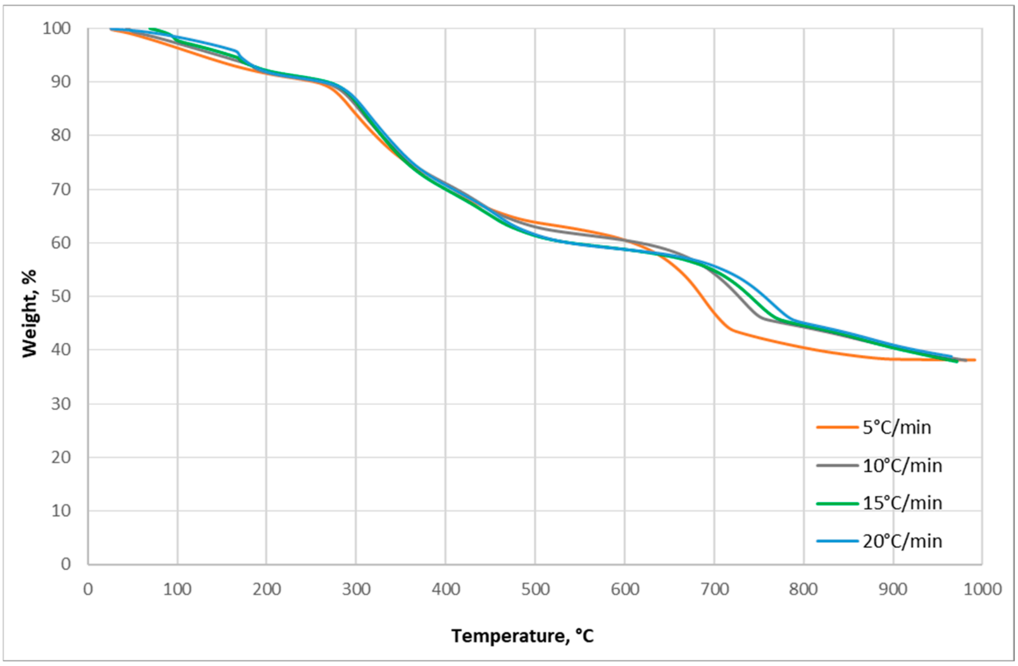

Figure 4. TGA curves of casein at different heating rates.

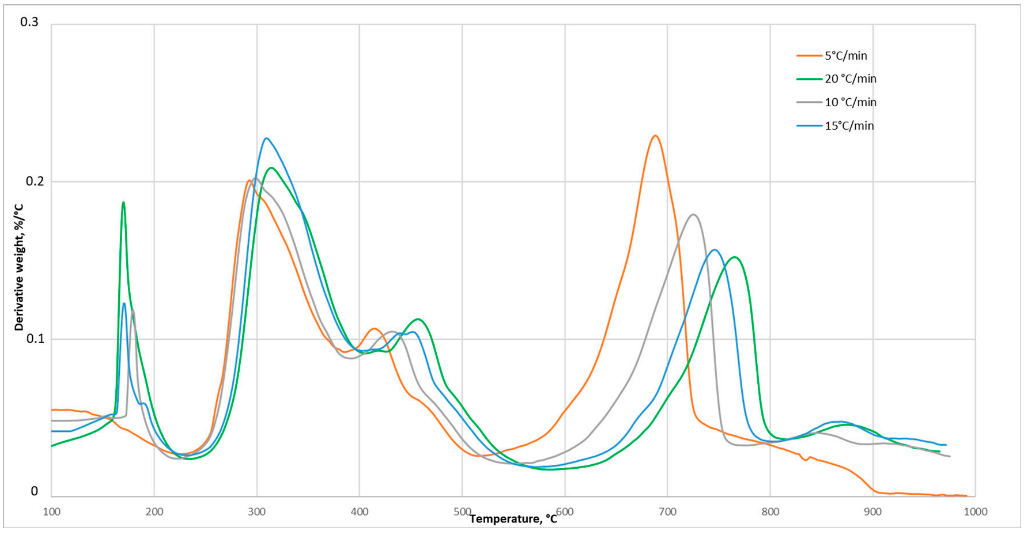

Figure 5. DTG curves for casein.

One should observe that casein degradation starts at a temperature of around 175 °C and ends at a high temperature in the range 590 °C–800 °C, with a final weight residual of 37.9% at 900 °C due to the release of the gaseous substances CO_2, CH_4, NH_3, and HNCO, with the expected formation of an intermediate byproduct which is eliminated in the last stage.

Table 3. TGA results for neat casein system (Test at 10 °C/min).

Temperature Range, °C	Tmax, °C	Weight Residual, %	Maximum Degradation Rate, %/°C
177–208	186.1 ± 0.5	93.43 ± 0.2	0.1180
252–389	303.6 ± 0.8	84.85 ± 0.4	0.2018
410–462	437.5 ± 0.9	67.46 ± 0.3	0.1047
590–765	730.9 ± 0.5	49.39 ± 0.1	0.1790

To obtain more information without any assumption on the thermal degradation mechanisms, the Kissinger kinetic analysis was employed for the decomposition stages above 200 °C. By the Kissinger method, the variations in the dynamic TGA data are analyzed through the changes in run heating rate, β, as a function of the maximum peak temperatures, Tmax, in the DTG curves. The activation energy can be calculated from the plot of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate by the equation:

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \frac{E}{RT_{max}}$$

where β is the heating rate, Tmax is the absolute temperature (K), Ea is the activation energy, and R is the gas constant (8314 J/kmol). Hence, the activation energy Ea can be calculated by the curve slope of the of $\ln(\beta/T^2max)$ vs. 1/Tmax. Figure 6 reports the Kissinger method applied to TGA data relative to the second decomposition stage occurring between 250 and 390 °C. The linear fitting is based on four computed points, one for each heating rate, and the R-squared value result was equal to 0.9915.

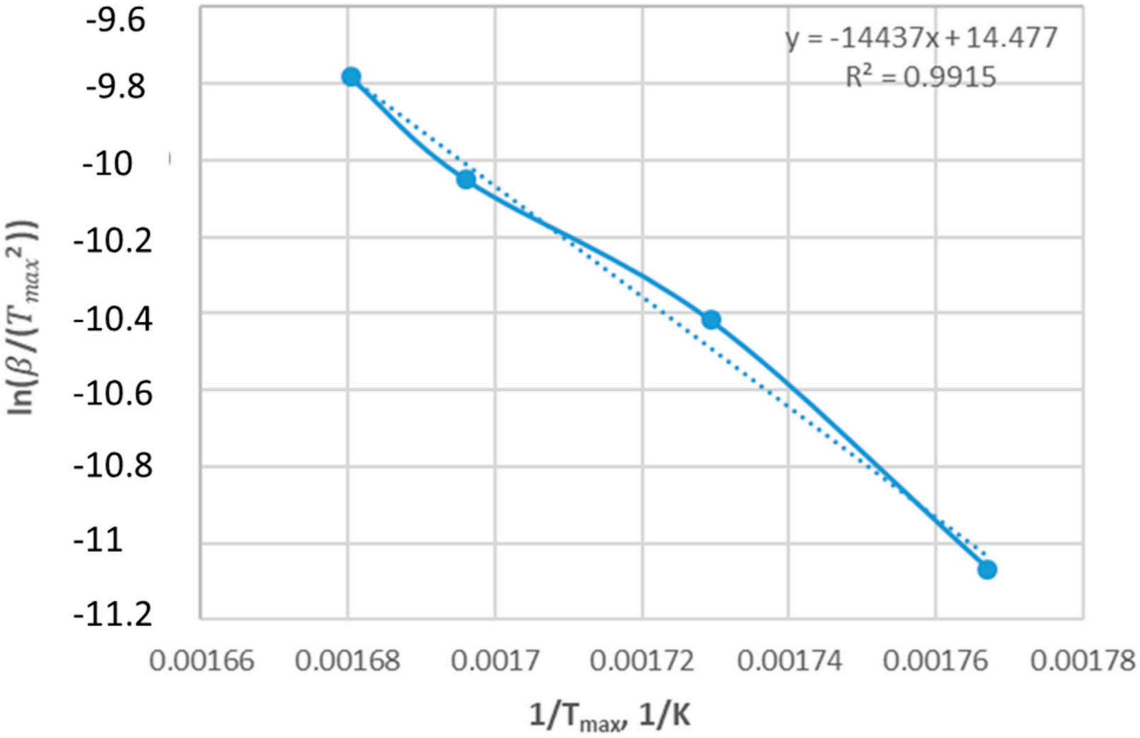

Figure 6. Kissinger model applied to the casein TGA data for the second degradation step.

Table 4 shows the estimated degradation activation energies for the neat casein.

Table 4. Activation energies for the casein system.

Temperature Range, °C	E, KJ/mol
250–390	120.03
390–470	115.97
550–800	132.30

TGA tests at different heating rates were also performed on all chitosan and dextrose formulations under nitrogen atmosphere at 10 °C/min. Figures 7 and 8 show the DTG curves for the formulations including 50%*w*/*w* of the sugars. It is possible to notice a simpler pathway decomposition for the chitosan formulation [29] that decomposes in three main stages and has a 50% weight loss at 405 °C. Both sugars affect the degradation mechanisms of casein by significantly lowering the rate of the thermal degradation at high temperatures when the decomposition rate is significantly reduced, as reported in Table 5, where the TGA data for all analyzed formulations are reported for the last decomposition stage, occurring almost between 600 °C and 800 °C.

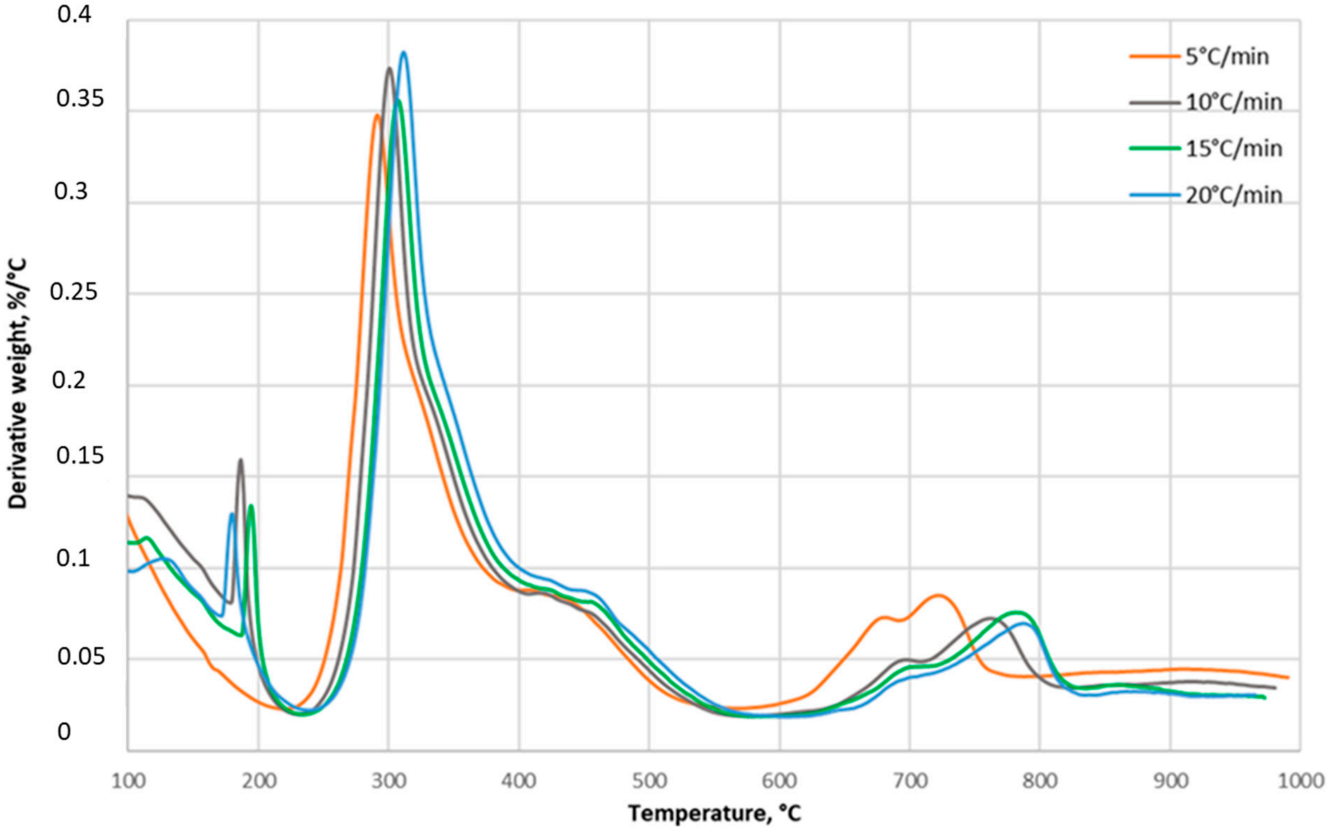

Figure 7. DTG curves of chitosan (50%*w*/*w*) formulation under nitrogen atmosphere at different heating rates.

The behavior of the dextrose-based formulation [30] is more complex and shows a large degradation plateau with a low rate in the last decomposition stage. A clear water desorption at temperatures below 200 °C for all heating rates is observed. Kissinger analysis was also performed for the saccharides formulation materials in the main temperature range between 200 and 400 °C, where the loss weight is more significant, evaluating activation energies higher than that of casein system (see Figure 9) In particular, the highest increase is associated with dextrose formulation with 50% of dextrose, which is characterized by an activation energy equal to 235.31 KJ/mol. The addition of polysaccharides can induce the formation of intermolecular bonds with casein, such as hydrogen bonds and electrostatic interactions, which make the system more resistant to thermal degradation. This means that more heat is required to break down these interactions before thermal decomposition begins demonstrating the efficiency of sugars for the mitigation of casein thermal degradation.

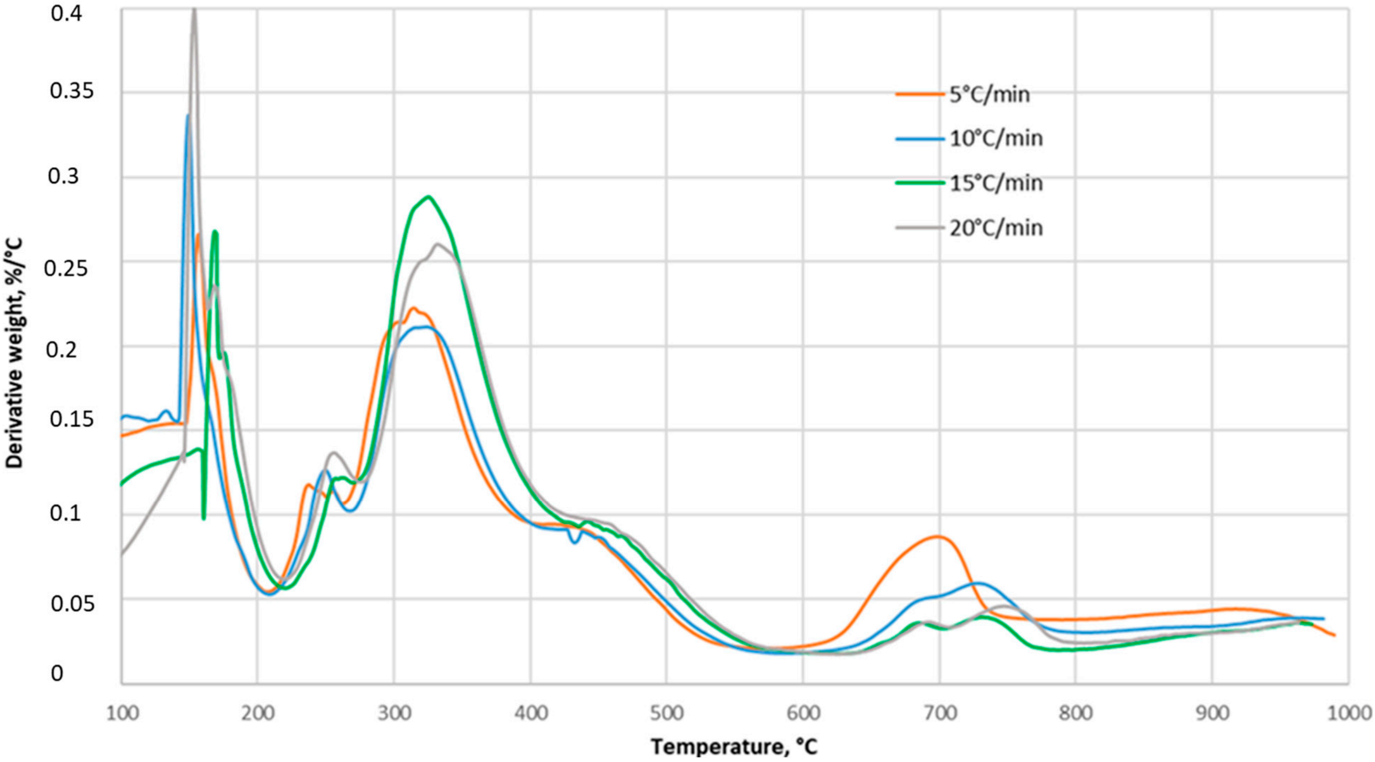

Figure 8. DTG curves of dextrose (50%w/w) formulation under nitrogen atmosphere at different heating rates.

Table 5. TGA results for the sugar-modified casein systems (Test at 10 °C/min).

Material	Tmax, °C	Maximum Degradation Rate, %/°C	Final Residual at 900 °C
CH10	737.2 ± 0.5	0.09366	33.74 ± 0.3
CH20	734.8 ± 0.2	0.11141	33.15 ± 0.1
CH30	757.1 ± 0.8	0.09332	30.87 ± 0.2
CH40	737.8 ± 0.7	0.08546	29.46 ± 0.1
CH50	761.9 ± 0.5	0.07258	28.07 ± 0.2
DX10	694.8 ± 0.2	0.06851	30.62 ± 0.4
DX20	684.6 ± 0.2	0.07948	34.39 ± 0.3
DX30	700.9 ± 0.5	0.07226	36.97 ± 0.2
DX40	706.6 ± 0.3	0.09081	34.78 ± 0.2
DX50	730.1 ± 0.7	0.05932	24.34 ± 0.3

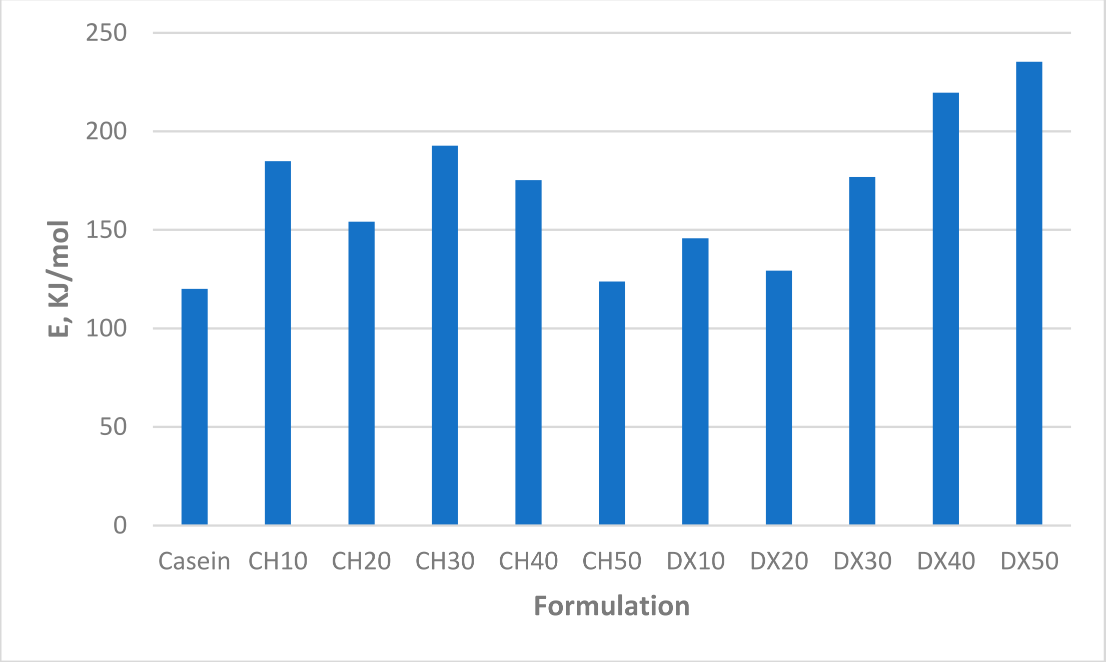

Figure 9. Activation energies for all analyzed formulations in the main temperature-degradation stage.

3.2. Spectroscopic Analysis

FT-IR analysis has been performed to investigate the potential chemical interaction between the casein and the polysaccharides with the highest content (50%*w*/*w*). The FT-IR spectra relative to the casein, the CH50, and the DX50 materials are shown in Figure 10, while Table 6 reports the main peaks and the corresponding band of the FT-IR spectra obtained for the casein at environmental temperature.

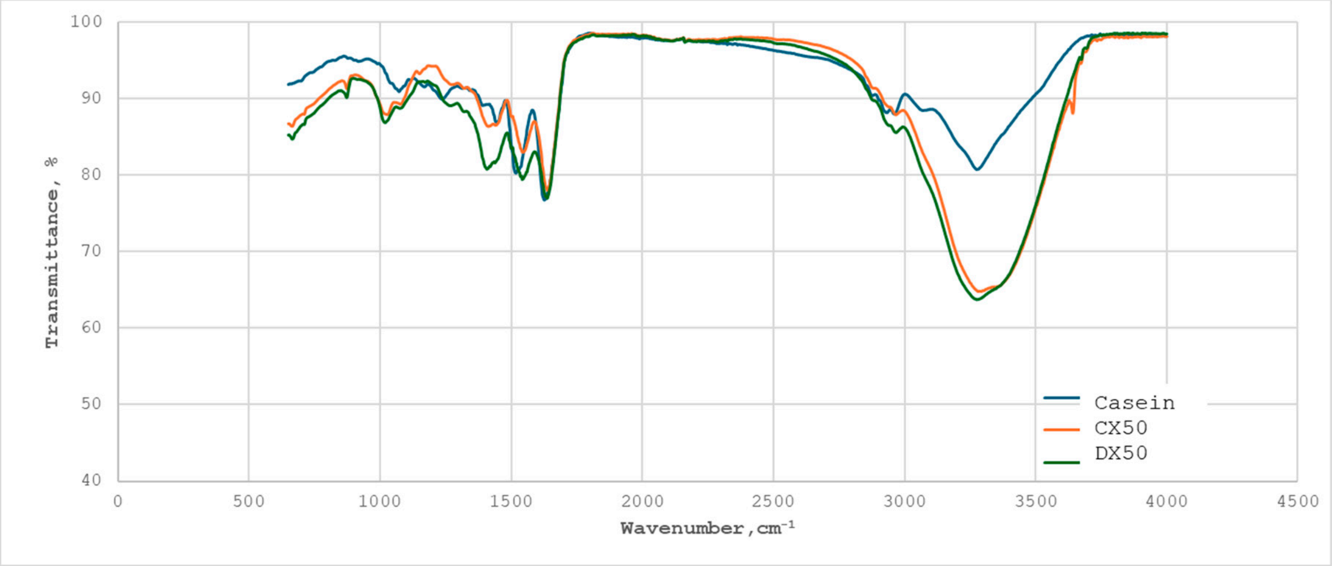

Figure 10. FT-IR spectra of casein, CX50 and DX50 materials.

In the case of the casein [31,32], the observed strong band between 3200 cm^{-1} and 3400 cm^{-1} denotes the presence of the hydrogen bonds. The peaks at 1650 cm^{-1} and at 1540 cm^{-1}, relative to Amide I and Amide II, respectively, reflect the peptidic nature of casein and are typical of secondary proteins. The peaks between 1230 cm^{-1} and 1300 cm^{-1}

can be ascribed to phosphates. The peaks between 1000 and 1200 cm^{-1} are linked to C-N and C-O bonds, relative to lateral amino acid residues.

Table 6. Fourier transform infrared spectroscopy data for the neat.

Band, cm^{-1}	**Assignment (25 °C)**
3200–3400	Stretching O-H e N-H
1650–1660	C=O stretching (Amide I)
1530–1550	N-H bending + C-N stretching (Amide II)
1400–1450	C-H bending e COO$^-$ stretching
1230–1300	P=O stretching (phosphates)
1000–1200	C-O stretching, C-N stretching
<900	Fingerprint region

Further, from Figure 10, it is possible to observe that both the chitosan CH50-based and dextrose DX50 materials are characterized by a strong band between 3200 cm^{-1} and 3400 cm^{-1}. However, the CH50 peaks in the range 1000–1200 cm^{-1} are more pronounced than those of DX50 material, outlining a stronger interaction between casein and chitosan due to the C-O-C bonds of chitosan. Thus, chitosan interacts more strongly with casein, forming hydrogen and ionic bonds, while dextrose, being a monosaccharide without amino groups, should form weaker bonds and slighter variations in the FT-IR spectrum. However, dextrose has simpler molecular structure and should provide more thermal stability to casein.

3.3. Flammability Behavior

Vertical flammability tests were carried out according to the ASTM D3801 standard [33] on five samples having a length of 125 ± 5 mm, width of 13 ± 0.5 mm, and thickness in the range from 0.025 to 13 mm. Each specimen was mounted by using a clamp, with the longitudinal axis positioned vertically. The lower end of the sample was placed 300 ± 10 mm above a cotton pad, which served to detect any material dripping. After securing, the sample was exposed to the flame at a distance of 10 mm for 10 s, as illustrated in Figure 11.

Figure 11. Vertical flammability test setup according to ASTM D3801.

After the removal of the flame, the time during which the sample continued to burn was recorded as the first "after flame" time (t1). Once the flame was extinguished, the test was repeated to obtain the second "after flame" time (t2). Table 7 summarizes the results of these tests.

Table 7. Results of the "after flame" times t1 and t2 for the tested samples.

Sample	t_1 (s)	t_2 (s)
RB	34.1	0
CH50	33.3	0
DX50	8.02	0

Figure 12 shows a picture of the three analyzed samples that were characterized by the burn marks along the cut edges. This depends on the material delamination, induced by the cutting process. Thus, along the cut section, the flame spreads more easily.

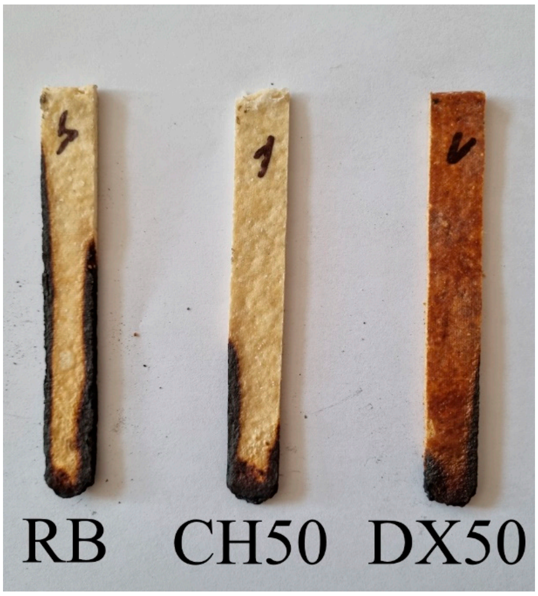

Figure 12. Burn marks observed on the samples after testing.

During testing, none of the samples exhibited dripping, and the cotton remained unburned. Based on the results presented in Table 7, the dextrose-based casein material can be classified as V-0, as its "after flame" time was below 10 s. On the other hand, the casein samples and those with chitosan can be classified as Class V-1, since their "after flame" times exceeded 30 s. These results are confirmed also by the evaluation of the total "after flame" time (t1 + t2). For the casein and chitosan samples, the total time was less than 250 s, denoting a Class V-1 classification. In contrast, the samples with dextrose exhibited a total "after flame" time of less than 50 s, supporting the classification as V-0.

In addition to the proposed evaluation, a statistical analysis was performed on the after-flame times measured by the flammability tests. One-way ANOVA revealed a statistically significant difference between the groups (F = 16.74, p = 0.0035), indicating that adding different additives to casein significantly affects its flammability behavior. To determine which formulation statistically differs from the others, Tukey's post hoc test was conducted. The results (see Table 8) show that the addition of both chitosan and dextrose significantly lowers after flame times compared to pure casein. This confirms that the addition of polysaccharides effectively enhances fire resistance.

Table 8. Tukey's post hoc test results for after-flame times.

Group 1	Group 2	*p*-Value
Casein	Casein + Chitosan	0.006
Casein	Casein + Dextrose	0.009

4. Conclusions

A casein glue has been prepared and modified by the addition of two different polysaccharides, chitosan and dextrose, at different concentration levels, in order to reduce shrinkage phenomena related to the water evaporation during the drying. Results evidenced a positive effect both for chitosan and dextrose base materials. The CH50 system, based on 50%w/w of chitosan, exhibited the smallest weight and diameter percentage changes. Further, the thermogravimetric TGA characterization and Kissinger analysis evidenced a reduction in the degradation rate at temperatures above 600 °C and an increase in degradation activation energy of up to 60% and 96% for the chitosan and dextrose materials compared to the neat casein in the temperature range between 250 °C and 400 °C. In addition, FT-IR analysis confirmed that both chitosan and dextrose interact with casein by forming hydrogen bonds, providing more resistance to thermal degradation. Finally, vertical flammability tests evidenced that chitosan and dextrose enable the improvement of casein flammability behavior by reducing the "after flame" time. Thus, this preliminary study demonstrated that chitosan and dextrose could be efficient and sustainable additives to control and mitigate the thermal decomposition and degradation mechanisms of casein glues.

Author Contributions: Conceptualization, M.R.R. and A.L.; methodology, All; software, M.R.R.; validation, All; formal analysis, M.R.R., V.A. and A.L.; investigation, All; resources, All; data curation, V.A.; writing—original draft preparation, M.R.R. and V.A.; writing—review and editing, all; visualization, all; supervision, A.L.; project administration, M.R.R. and A.L.; funding acquisition, M.R.R. and A.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received funding by the Ministry of Research under the PRIN 2022 PNRR: "Manufacturing of composite materials casein-based: New frontiers for sustainability—MaCoSu" with the identification code: P2022KYCY9.

Data Availability Statement: Data will be available on request.

Acknowledgments: The authors gratefully acknowledge Mario De Angioletti, Maria Rosaria Marcedula, Fabio Docimo, (CNR-IPCB) for the technical support provided to this research.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

RB	Casein base matrix
CH10	Casein with 10 wt% chitosan
CH20	Casein with 20 wt% chitosan
CH30	Casein with 30 wt% chitosan
CH40	Casein with 40 wt% chitosan
CH50	Casein with 50 wt% chitosan
DX10	Casein with 10 wt% dextrose
DX20	Casein with 10 wt% dextrose
DX30	Casein with 30 wt% dextrose

DX40	Casein with 10 wt% dextrose
DX50	Casein with 50 wt% dextrose

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