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The Initial Development and Evaluation of Cross-Linked Casein Films for Sustainable Footwear

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Abstract: To increase the sustainability of footwear and align it with the circular bioeconomy, there is a pressing need to develop novel bio-based materials to replace the synthetic polymers currently used. In this study, casein-based films were prepared by solution casting with a tannic acid cross-linker, and a glycerol plasticizer. The properties important to footwear materials were characterised, including tensile strength and elongation, stitch strength, hardness, grain cracking strength, water vapour permeability, and thermal properties. The tannic acid imparted a brown colour to the films with good resistance to light-induced fading. Their tensile strengths were 4–5 N/mm^2, elongation at break 45%–73%, and water vapour permeability 0.2–0.6 mg/(cm^{2}h), depending upon the levels of the cross-linker and plasticiser. The strength of the films was close to those of some non-leather footwear materials such as compact rubbers and insock materials, but below that required for leather shoe vamps/uppers. The casein films were successfully used in sneaker- and ballerina-style shoes as components of the insock and decorative design elements on the vamp. This work has demonstrated the concept of using casein films in footwear. The properties of the films could be improved by further research, particularly with respect to cross-linking, plasticizing, and combining with bio-based fibers and fabrics.

Keywords: biopolymers; footwear; casein; leather; circular bioeconomy; tannic acid; microplastics; cross-linking; plant polyphenols; regenerated protein

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1. Introduction

Worldwide footwear consumption has increased rapidly over the last 40 years and the rate was around 20 billion pairs in 2005 [1]. It is estimated that in the EU alone, the waste arising from post-consumer shoes will soon exceed 1.2 million tonnes per year [2]. Leather has been used in footwear, jackets, hats, belts, and bags for millennia. Over the last 50 years, synthetic polymer materials have partially replaced leather in some of these products; for instance, around 70% of footwear is now made with synthetic materials and substances [3], including films of polyurethane, ethyl vinyl acetate, and polyvinyl chloride, adhesives, solvents, dyes, and fibres. The large number of shoes produced each year means that huge quantities of these synthetic materials are entering the environment both in shoes and in waste from shoe manufacturing. For instance, the amount of ethyl vinyl acetate waste/off-cuts produced by the global footwear industry has been estimated as 190,400 tons per annum [2].

The synthetic polymers used are not single materials and contain many additives including plasticisers, fillers, activators, and stabilisers. The emerging understanding of sustainability and the negative effects of some of the synthetic polymers encountered in many products, including footwear, is causing more and more people to become concerned about these materials. Perhaps the greatest concern is around their possible effects on human health, as some synthetic polymers, such as polyvinyl chloride, polyester, and polycarbonates contain toxic compounds, e.g., phthalate plasticisers, antimony, and Bisphenol A, respectively [4]. Such concerns are reasonable, as these materials are in contact with our food, drink, and skin [5], and there is often an appreciable delay between the identification of a hazard and legislative protections being implemented. Another area of concern is the accumulation of synthetic polymers (including their additives) in the environment. or example, zinc pollution on steppingstones at Pompeii has been attributed to tourists' footwear [6].

Over the last ten years, an understanding has emerged of the threat posed by microplastic pollutants in the air, land, water, and food chains [7–9]. The recycling of synthetic polymers, as practised, has some benefits, but can increase consumers' exposure to toxins; for instance, there is evidence that consumer products (such as toys) contain polymers from recycled electronic casings, which are of necessity for their original use, and they contain high levels of metallic and halogenated flame retardants [4]. Another concern with synthetic polymers is that they consume petrochemicals and therefore exacerbate pressure on finite natural resources and demand/supply conflicts [10].

Circularity and the bioeconomy are two important concepts in sustainability, which are being addressed in many areas, from household waste to the preservation of cultural heritage [11,12]. A circular bioeconomy, which has sustainability and circularity at its heart, will lead to the modernisation of production systems, protection of the environment, and the enhancement of biodiversity [11–13]. The circular bioeconomy is a process of dynamic and complex social transformation which not only aims to reduce the environmental impacts of resource use but also takes a systems approach for economic, social, and environmental sustainability. It offers a unique opportunity to comprehensively address interconnected societal challenges such as food security, the scarcity of natural resources, the dependence on fossil resources, and climate change while ensuring sustainable economic development.

The concerns about the effects of synthetic materials on health and the environment, coupled with a desire to enact a circular economy, are driving interests in bio-based materials that are renewable, biocompatible, and biodegradable [14,15]. The demands of informed consumers will not be allayed by greenwashing or manipulation of sustainability indices (e.g., discredited claims of biodegradability) [16]. Astute manufacturers are increasingly using bio-based materials [13–19]. For example, wool is used in NASA's Orion spacecraft to protect astronauts from fire [20], and in face masks, building insulation [21], and industrial catalysis [22,23].

The leather industry has improved sustainability with innovations such as chrome-free tannage, enzymatic depilation, and consideration of circular economy principles [24–28]. New biomaterials have been used commercially in footwear, such as wool and mycelium [29,30], but most shoe materials are still synthetic polymers, and the recycling of many types of modern footwear is practically impossible because they are constructed from a diverse mixture of synthetic materials.

As leather is a proteaceous bio-based material, developments in reconstituted proteins are highly relevant to the footwear materials of the future. Reconstituted protein materials are not new, having been used before the development of synthetic polymers, and early examples include casein fibres, buttons and jewellery (Lactoloid and Galalith), peanut protein fibres (Ardil), and zein protein fibres (Vicara) [31,32]. Interest in the circular bioeconomy is reviving interest in reconstituted protein materials, especially when re-engineered with modern green chemistry approaches [33–39] and at least one new product has been commercialised, namely Qmilch casein fibres [40]. Most cross-linked casein materials are biodegradable [10,40].

Casein is most often encountered in cheese, dietary supplements, glues, paints, and intumescent fire retardants. Casein is a group of four phosphoproteins, comprising approximately 80% of the proteins in cows' milk [41]. Casein can form complex polymeric aggregates that interact through hydrophobic, electrostatic, and calcium interactions [42], which provide opportunities for manipulation into useful forms. Casein proteins are strongly attracted to each other, which results in stiff, brittle films [43] unless plasticisers and cross-linkers are employed. Proteins can be cross-linked by radiation, heat, enzymes, and compounds such as glutaraldehyde and tannic acid [44–47]. Significant research has been made into casein-based coatings for application to footwear materials [48] and food packaging [49], but not into stand-alone components of footwear to replace leather/synthetics.

Tannic acid is the archetype of protein cross-linkers and lends its name to the process of cross-linking the collagen in animal skins—tanning (Figure 1). Tanning imparts strength and durability to water, microbes, and heat [50,51]. The antioxidant properties of tannic acid are beneficial in footwear as they may counteract odour-causing bacteria and pathogenic fungi such as those that cause athlete's foot [35,52].

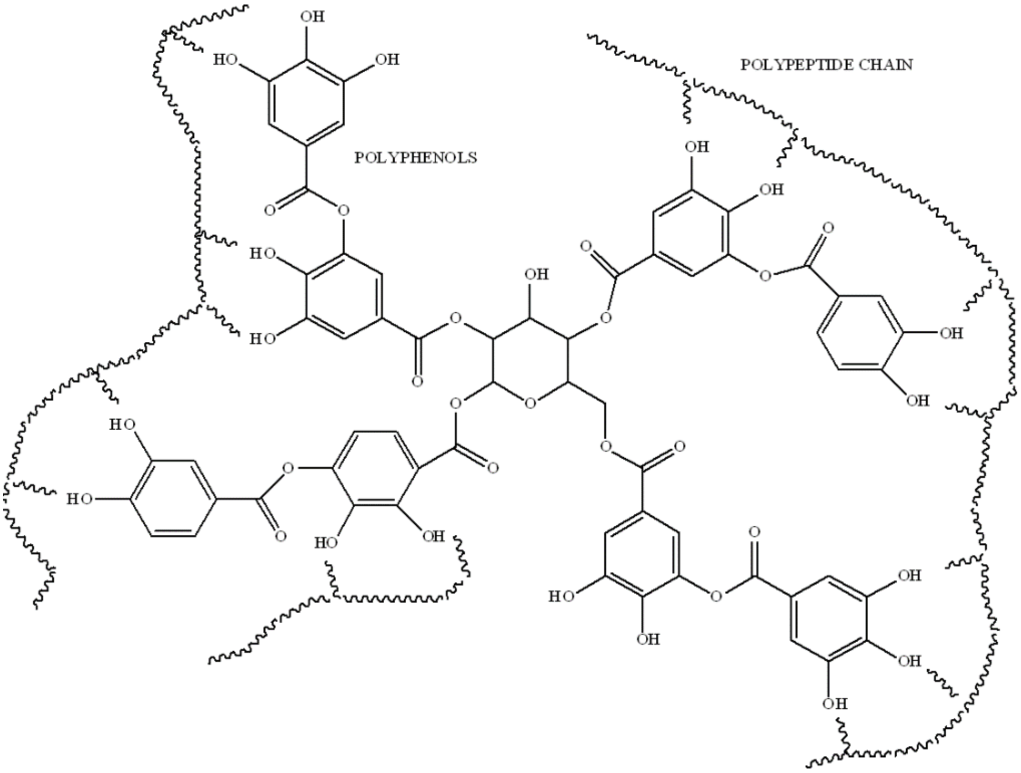


Figure 1. Interaction of phenolic acid with the chains of polypeptides (pp).

The aim of the work reported here was to prepare casein films and incorporate them into footwear, specifically shoes. To the best of the authors' knowledge, this is the first such study. The casein films were prepared with different levels of tannic acid cross-linker and glycerol plasticiser [49]. The properties important to footwear manufacturing and moisture transmission were determined, to evaluate the films' potential as a sustainable component of footwear. Infra-red spectroscopy was performed to assess cross-linking.

2. Materials and Methods

2.1. Preparation of Films

Casein solutions (10% *w*/*w*) were prepared by gradually adding casein (bovine, technical grade, >95%, Acros Organics, Waltham, MA, USA) to a solution of sodium hydroxide (1% *w*/*w*), (97%, Sigma-Aldrich) with stirring at room temperature. Tannic acid (95%, Acros Organics), which had been pre-dissolved in the minimum amount of sodium hydroxide solution (1% *w*/*w*) was then added to the casein solution, at two different levels, see Figure 2.

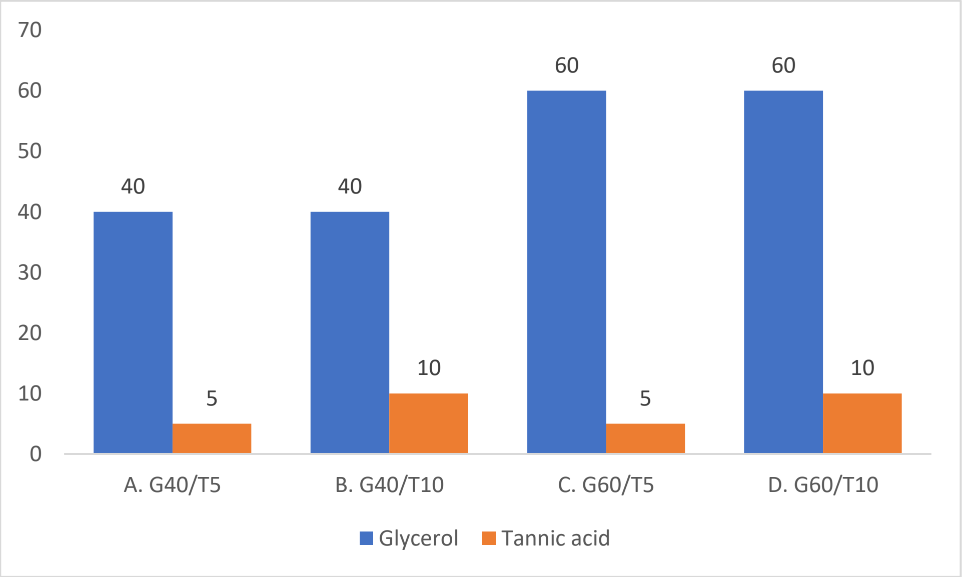


Figure 2. Summary of films prepared, showing levels of tannic acid and glycerol as mass percentages of casein.

To facilitate the reaction between casein and tannic acid, the casein-tannic acid solutions were aerated for three hours at room temperature, with mechanical stirring, see Figure 1. Significant amounts of a stable brown foam were produced, which was manually removed. Glycerol (Analar grade Labserve, Thermo Fisher, Waltham, MA, USA), was then added at two levels (see Table 1), and the solutions mixed for 5 min then deaerated in a vacuum oven (20 °C, 30 kPa of vacuum, 1 h). The solutions were then cast into square polystyrene dishes of either 100 or 529 cm^2, at 0.5 g/cm^2, then dried at 20 °C, 50% relative humidity (RH), in an incubator (Binder) for several days. The resulting films were 900 g/m^2 at 20 °C, 50% RH.

Table 1. Colours of films and their resistance to light-induced fading [1].

Film	L*	a*	b*	Lightfastness
A. G40/T5	15.0	4.0	−0.9	4.17 ± 0.29 [a]
B. G40/T10	25.5	0.3	5.3	4.17 ± 0.29 [a]
C. G60/T5	6.9	3.2	−2.1	4.17 ± 0.29 [a]
D. G60/T10	27.1	3.2	7.5	4.00 ± 0.00 [a]

[1] 4 and 3 replicates made for colour and lightfastness measurements, respectively; [a] Different letters in the same column indicate significant differences ($p < 0.05$).

To provide a reference material for infrared spectroscopy (Section 3.5), a film of casein alone was prepared by casting a 10% *w/w* solution (in 1% *w/w* sodium hydroxide), without aeration and deaeration. This film was very brittle.

2.2. Characterisations

2.2.1. Color and Resistance to Light-Induced Fading

The colors of the films were measured with a spectrophotometer (Colour-guide 45/0, Mahlo), with D65/10 illuminant/observer, in the Commission International de l'Eclairage, L*a*b* color space. Where L* is the perceived lightness and covers a range from white (100) to black (0), and the a* and b* coordinates are related to Hering's opponent theory and represent hues on scales of red verses green (a*) and yellow verses blue (b*). Each measurement was made on four thicknesses of the same film laid on top of each other, to prevent reflection from the material on which the films were sitting. Four measurements were made of each film, and the results were averaged.

The resistance to light-induced fading (i.e., colour fastness to light, lightfastness) was measured with a Xenotest Alpha+ instrument (Atlas) in accordance with a standard method (ISO 105-B02) [53]. This method is intended for determining the resistance of the colour of the material to the action of a standard artificial light source representative of natural daylight. The side of the films to be tested (45 mm × 10 mm) was exposed to light from a Xenon lamp, under controlled conditions, along with eight blue dyed wool standards (Blue Scales [53]). The light fastness was assessed at different times, by visual comparison of the fading of the films with the fading of dyed wool standards, until the films had undergone a colour change of grey scale grade 4.

2.2.2. Mechanical Properties

The mechanical properties of the films that are important to footwear materials were determined by standard test methods that are widely accepted by the footwear industry internationally. Determination of tensile strength and percentage elongation, Determination of tear load, (single edge tear), and measurement of stitch tear resistance tests were conducted by using a tensile testing machine with a force range appropriate to the specimen under test, a 5 kN load cell, interchangeable jaws to hold the samples, and a uniform speed of separation of the jaws of (100 ± 20) mm/min [54–56]. Determination of the distension and the strength of the surface was measured with a lastometer, pushing a metal ball through the center of a clamped circular leather sample according to standard method ISO 3379 [57]. The hardness of the films was determined by the durometer method (Shore hardness) [58]. The thickness of the films was determined with a micrometer.

2.2.3. Equilibrium Moisture Content

The weights of samples of films were measured after 8 h in an oven at 80 °C (the "dry weight") and then after conditioning for 24 h in an incubator (Binder), with forced air circulation at 25 °C and various relative humidities between 20% and 80%.

2.2.4. Water Vapour Permeability

The water vapour permeability of the films was measured with STM 473 (SATRA) test equipment in accordance with a widely recognised ISO method 14268 [59]. Testing was performed in a conditioned room at 20 ± 2 °C and 65 ± 5% RH and was based on gravimetric calculation of the water vapour passing through the films (30 mm diameter) placed on covers of the test bottles filled with silica gel.

2.2.5. Fourier Transform Infrared Spectroscopy (FTIR)

The spectra of the films were captured on a Nicolet Summit Pro FTIR spectrometer with an Everest attenuated total reflectance attachment (Thermo Fisher, Waltham, MA, USA) over 4000–400 cm^{-1} at a resolution of 4 cm^{-1} averaged over 32 scans.

2.2.6. Statistical Analysis

The measurements were analysed for statistically significant differences by ANOVA and Duncan's test using a statistical software package (SPSS version 24). A significance level of 0.05 was used.

2.3. Preparation of Shoes

Selected casein films were incorporated into sneaker- and ballerina-style shoes (see Section 3.6 for further details). The shoes were made of box calf by the AGO cemented method (AGO—*Another Great Opportunity*). Films were applied to the shoe vamps by sowing or button fastening. The films were also incorporated in the insock, as the middle layer, between polyurethane foam, by gluing and sewing.

3. Results and Discussion

3.1. Appearance of the Films and Their Resistance to Light-Induced Fading

One of the films is shown in Figure 3; it was the only one that that was sufficiently transparent to allow the material underneath to be seen. The brown colour imparted by the tannic acid was similar to that of many leather shoe materials. Increasing the proportion of tannic acid from 5% to 10% made the casein film darker (i.e., reduced L*, lightness), Table 1. The lightfastness results of the various samples were not significantly different from each other and were all adequate for the footwear materials (Table 2) [60,61].

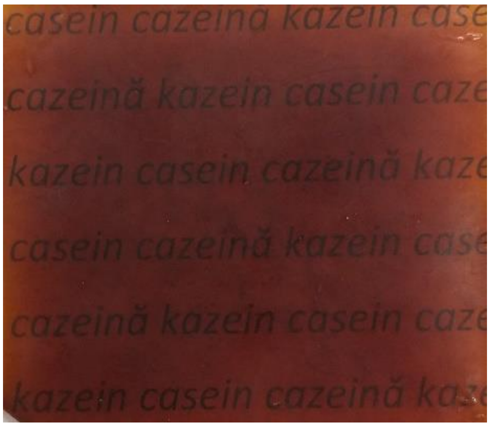


Figure 3. Casein film G40/T5 (9 cm × 9 cm).

Table 2. Thickness and tensile properties.

Film	n	Thickness (mm)	Tensile Strength (N/mm^2)	Elongationat Break (%)	Stitch Tear Strength (N/mm)	Single Edge Tear Strength (N/mm)
A. G40/T5	3	0.67 ± 0.01 ^{b}	4.38 ± 0.60 ^{a}	45.0 ± 10.6 ^{b}	4.80 ± 0.16 ^{c}	0.34 ± 0.05 ^{c}
B. G40/T10	3	0.65 ± 0.02 ^{b}	5.05 ± 0.31 ^{a}	51.6 ± 19.3 ^{a,b}	8.12 ± 1.40 ^{b}	0.67 ± 0.02 ^{b}
C. G60/T5	3	0.70 ± 0.07 ^{b}	4.39 ± 0.40 ^{a}	51.3 ± 7.4 ^{a,b}	7.81 ± 1.33 ^{b}	0.67 ± 0.02 ^{b}
D. G60/T10	3	0.87 ± 0.02 ^{a}	4.49 ± 0.35 ^{a}	73.2 ± 6.9 ^{a}	13.02 ± 1.04 ^{a}	1.79 ± 0.03 ^{a}

$^{a, b, c}$ Different letters in the same column indicate significant differences ($p < 0.05$).

3.2. Mechanical Properties

The tensile strengths of the films were similar to each other, with an average of 5 N/mm^2, (Table 2), which is below the recommended values of 20 for side upper leathers, 15 for lining leathers, and 10 for insock leathers [61]. The tensile strengths of the films were close to those of some non-leather footwear materials i.e., 5–8 for compact rubbers, 5–12 for non-leather insock materials, 8 for cotton lining materials, and 8–14 for polyvinyl chloride [61]. The percentage elongations at break of all the films are higher than the recommended value of 40% [61]. The stitch tear strength and single edge tear strength properties of the films can be ranked as Film A lowest, Film B and C average, and Film D highest, attributable to the levels of plasticiser and cross-linker. However, these values are below the recommended minimum for footwear materials of 25 N/mm for edge tear strength and 80 N for stitch tear strength [61]. Increasing the level of tannic acid from 5% of the casein to 10% doubled the stitch tear strength and single edge tear strength, regardless of the level of plasticiser, thus demonstrating the importance of tannic acid cross-linking to imparting strength. It can be concluded that the films do not meet the strength properties of the shoe materials but have adequate distension and elongation properties.

Increasing the level of tannic acid reduced both the shore hardness and the grain crack strength (Table 3). Grain distensions were higher than the recommended 7 mm for shoe upper leathers [61]. These results confirm that the tannic acid modifies the mechanical properties of the films, in line with the results for tear strengths presented in Table 2.

Table 3. Hardness and grain strength.

Film	**Shore Hardness** [1]		**Grain Crack** [2]		**Grain Burst** [2]	
	A	**D**	**Strength (kgf)**	**Distension (mm)**	**Strength (kgf)**	**Distension (mm)**
A. G40/T5	84.7 ± 6.6 ^{a,b}	67.6 ± 4.5 ^{a}	1.00 ± 0.00 ^{a}	10.89 ± 0.13 ^{a}	2.00 ± 0.00 ^{a}	11.61 ± 0.30 ^{a}
B. G40/T10	81.1 ± 2.3 ^{b}	60.4 ± 8.5 ^{b}	0.50 ± 0.00 ^{b}	10.91 ± 0.05 ^{a}	1.47 ± 0.50 ^{a}	11.57 ± 0.31 ^{a}
C. G60/T5	88.5 ± 3.4 ^{a}	62.9 ± 3.7 ^{a,b}	1.00 ± 0.00 ^{a}	11.07 ± 0.11 ^{a}	1.97 ± 1.00 ^{a}	11.84 ± 0.54 ^{a}
D. G60/T10	80.0 ± 7.2 ^{b}	61.0 ± 5.2 ^{b}	0.70 ± 0.26 ^{b}	9.32 ± 0.08 ^{b}	2.00 ± 0.00 ^{a}	11.40 ± 0.06 ^{a}

[1] $n = 10$; [2] $n = 3$; $^{a,\,b}$ Different letters in the same column indicate significant differences ($p < 0.05$).

3.3. Equilibrium Moisture Content

The films contained a large amount of moisture at high humidities, i.e., 50% at 80% RH (Figure 4), in common with leather. Only small differences were seen between the films, but they were consistent across the different relative humidities. Higher levels of glycerol gave higher moisture contents, which could reasonably be ascribed to its hygroscopicity. Inside a shoe, a footwear material's ability to absorb large amounts of water vapour increases the comfort of the wearer. High levels of moisture would not have any effect on the suitability of the material as a decorative element, see Section 3.6.

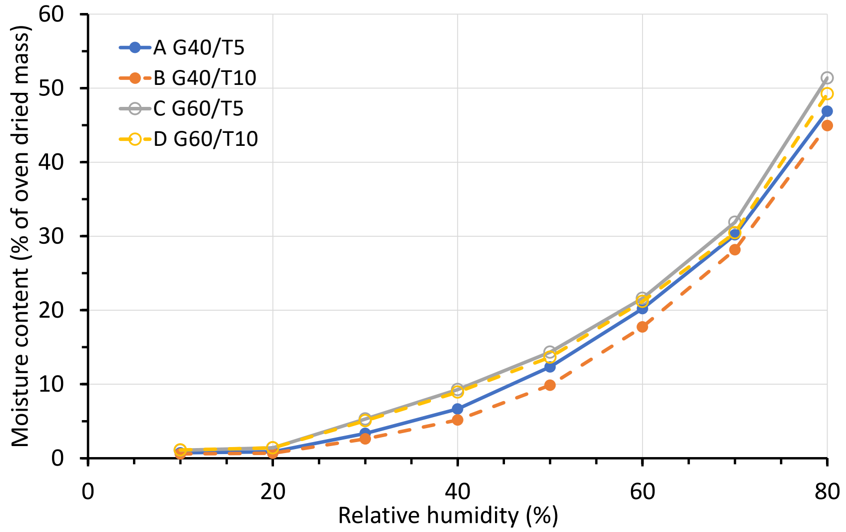
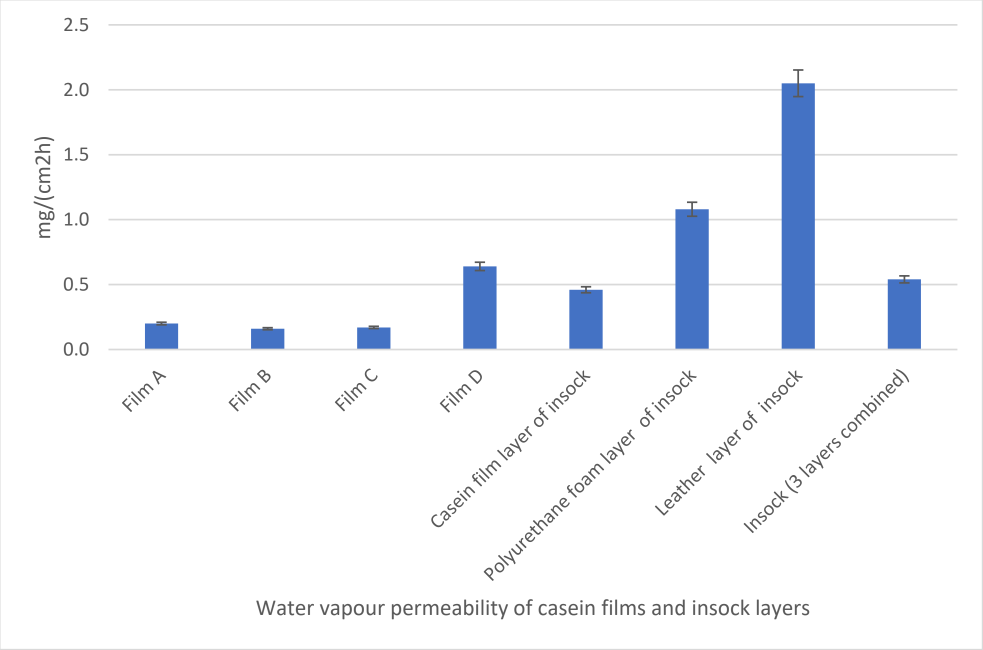


Figure 4. Moisture sorption isotherms of the casein films.

3.4. Water Vapour Permeability

The water vapour permeability (WVP) of shoe materials supports their comfort properties. The insock of the shoe contains three layers: casein film, polyurethane foam, and leather. The WVPs of the films, the layers of the insock, and the insock are determined separately and the results are shown in the Figure 5. Films B and C have a similar permeability, 0.16 and 0.17 mg/(cm^{2}h), respectively ($p > 0.05$). These values are below the required WVP of at least 0.8 mg/(cm^{2}h) [61,62]. Film D has around three-times greater WVP than the other films ($p < 0.05$) (i.e., 0.64 mg/(cm^{2}h)) and is closer to industry requirements; this may be due to the higher glycerol and tannic acid ratio of the D film compared to the other samples resulting in more cross-linking and the formation of more and smaller pores in the matrix structure of the film. Jankauskaitė et al. have found WVPs ranging from 1.16 to 3 mg/(cm^{2}h) on waterproof leather samples [62]. It is the combination of materials in a shoe that needs to be considered, and a 3-layer insock of casein, polyurethane, and leather was found to give an undesirably low permeability of 0.54 mg/(cm^{2}h). The WVPs of the casein film layer, the polyurethane foam layer, the leather layer of the insock, and all of the layers combined are found to be 0.46, 1.08, 2.05, and 0.54 mg/(cm^{2}h), respectively ($p < 0.05$).



Film A	Film B	Film C	Film D	Casein film layer of the insock	Polyurethane foam layer of the insock	Leather layer of the insock	Insock (three layers combined)
0.20 ± 0.01^{a}	0.16 ± 0.01^{b}	$0.17 \pm 0.01^{a,b}$	0.64 ± 0.04^{a}	0.46 ± 0.05^{C}	1.08 ± 0.07^{B}	2.05 ± 0.01^{A}	0.54 ± 0.06^{C}

[1] Determined from three replicates

$^{a,\,b}$ Different letters in the same row indicate significant differences ($p < 0.05$)

$^{A,\,B,\,C}$ Different letters in the same row indicate significant differences ($p < 0.05$)

Figure 5. Water vapour permeability of the casein films and insock layers (mg/(cm^{2}h)) [1].

3.5. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was performed to elucidate possible cross-linking between the casein and TA. The FTIR absorption band assignments of the films are shown in Table 4 and the spectra are presented in Figure 6. Incorporation of tannic acid shifted the amide I, II, and III bands, with the higher level giving the greatest shift. The size of the amide II peak was greatly reduced by 5% tannic acid and was very small with 10% tannic acid. These results show that there was covalent bonding (cross-linking) between the casein and the tannic acid, and these results are in line with previously reported FTIR results [49,63].

Table 4. FTIR absorption band assignment of the casein and casein–glycerol–tannic acid films (cm^{-1}).

Absorption Band	**Casein Only**	**A. G40/T5**	**B. G40/T10**	**C. G60/T5**	**D. G60/T10**
Bending vibrations of O–H and N–H	3276	3270	3270	3270	3278
Stretching vibrations of –CH_2	2959	2918	2917	2918	2916
Amide I, C=O stretching	1632	1626	1625	1633	1624
Amide II, N–H bending	1516	1539	1556	1542	1568
Amide III, C–N, N–H stretching	1237	1239	1242	1239	1245

3.6. Shoes

During the characterisation of the samples, it was observed that films B and D (i.e., those with the higher levels of tannic acid) were too stiff and brittle for use in uppers/vamp, presumably because of the higher level of cross-linking. Film C was slightly thicker than film B, but the effect of the flexibility was more important than the thickness.

Based on the results of the measured properties, different ways of incorporating the films into shoes were undertaken. Films A and C were applied as decorative elements on the vamp of two pairs of shoes. Due to the fact that film D had around three-times greater water vapour permeability than the other films, it was inserted in the insock of the shoes. The shoes are shown in Figure 7.

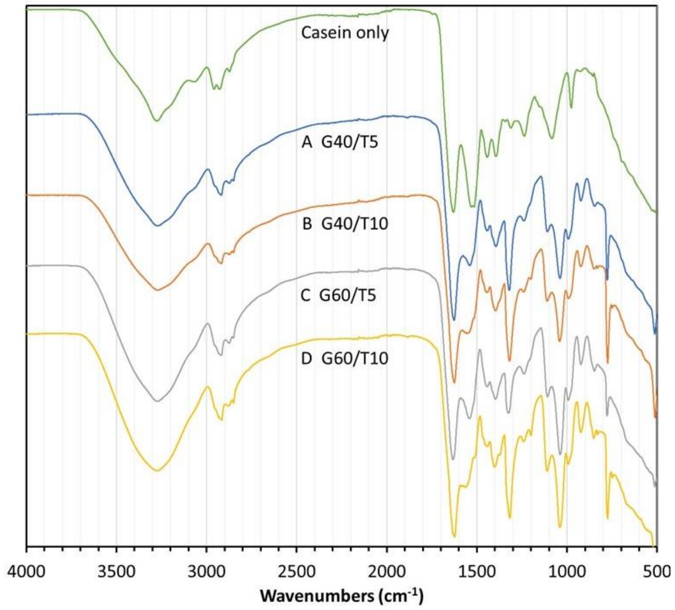


Figure 6. FTIR spectra of the films.


(**a**) (**b**) (**c**) (**d**) (**e**) (**f**)

Figure 7. Incorporation of casein films into shoes: (**a**) and (**b**) G40/T5; (**c**) and (**d**) G60/T5; (**e**) and (**f**) G60/T10, middle layer.

4. Conclusions

Films of casein were prepared using tannic acid as a cross-linker and glycerol as a plasticiser. The brown colour imparted by the tannic acid had good resistance to light-induced fading. The films had appreciable mechanical strength, (tensile strength 4–5 N/mm^2, elongation at break 45%–73%), extensibility (extension at break 45%–73%), and permeability to water vapour (0.2–0.6 mg/(cm^{2}h)). The tannic acid was shown to be cross-linking the casein and would thus contribute to the mechanical strength. The films contained high levels of moisture when exposed to high relative humidities, suggesting they would be valuable for the inner parts of shoes where they could help keep the wearer's feet dry and comfortable by absorbing perspiration.

The strength of the films was close to those of some non-leather footwear materials such as compact rubbers and insock materials, but below that required for leather shoe vamps/uppers. However, further research is likely to improve these properties. The resistance of the casein films to mold and bacteria also warrants investigation, particularly with respect to tannic acid's microbial resistance. Replacing glycerol with other plasticisers might significantly enhance the properties of the films. Another approach to increasing the strength of casein films is to combine them with other bio-based materials such as microcrystalline cellulose.

The high moisture content of the films at moderate relative humidities is advantageous for insock materials, but not for outer materials. The changes to cross-linking and plasticization discussed above in connection with mechanical strength could also be employed to reduce moisture content for casein films intended for the outer parts of shoes. An additional strategy warranting research is to incorporate fatliquors or natural hydrophobic materials into the films.

Casein films were successfully used as shoe materials, both as decorative design elements on the vamp and as a functional component of the insock. This work has thus shown that casein films are a promising bio-based material for footwear, which might replace synthetic polymers and thereby improve the sustainability of the 20 billion pairs of footwear produced every year and contribute to the realisation of a circular bioeconomy.

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