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The Use of Copper Phthalocyanine Pigments as Blue Colorants in Gelatin Films for Aquatic Food Packaging

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Abstract

In this study, Copper (Cu) phthalocyanine pigments, coded PD1 and PD2, were characterized, and the possibility of using them as blue colorants in gelatin-based materials for aquatic packaging was evaluated. Synthesized phthalocyanine pigments were compared with imported commercial PB15:1 (control) in terms of Fourier Transform Infrared Spectroscopy (FTIR), high-performance liquid chromatography (HPLC) results, Cu, and ash content. It was found that the synthesized PD1 and PD2 samples were the ones closest to the commercial powder in terms of FTIR peaks, Cu amount, and HPLC results. The selected sample coded PD1 at 0.5 wt% with respect to the solution was further added to gelatin-containing solutions containing 10% and 5% glycerol, and dried films of GL10 and GL5 were obtained, respectively. Although the 10% glycerol-added film showed better color properties, L, a, b, Hue angle, and Chroma parameters were insignificant ($p>0.05$). Tensile tests and creep/recovery curves showed that GL10 had 107% higher elongation at break, 29% lower Young's modulus, and higher strain values compared to GL5, making it softer and more flexible. Deformation parameters such as hardness, chewiness, and gumminess were also compared at different deformation rates for the selected GL10 sample. Results indicated that blue pigment-added gelatin films can be used in aquatic food product packages.

1. Introduction

1.1. Importance of Phthalocyanine for Packaging

Since the blue color is commonly used on packages of seafood products, its use in packaging materials for aquaculture has been increasing. Blue color may give associations with water, sea, and ocean, and could evoke feelings of trust, honesty, calmness, and security [1, 2]. It may also help create a brand identity that consumers associate with freshness and quality, and can be used to convey a message of trustworthiness in the product. Hallez et al. [3] stated that blue color-based package designs may lead to higher health perceptions for consumers [4]. Because of its association with water and freshness, it may be effective for aquaculture packaging materials. In 2024, the Marine Stewardship Council released specific guidelines for using the blue label in packages to ensure consistency, trust, and recognition among consumers for certified aquatic products [5–10]. Therefore, blue color pigments in aquatic food product packages will be important to ensure quality, appeal, and consumer satisfaction with the continued expansion of sales [6–9, 11].

Phthalocyanines are compounds with a structure similar to porphyrins that are naturally found in molecules such as chlorophyll and hemoglobin, with a central cavity large enough to accommodate more than 70 metals and metal ions [12, 13]. Despite their porphyrin-like structure, they are synthetic compounds that are not naturally found [14]. Phthalocyanine was first obtained in 1907 by Braun and Tschernak as a by-product during the synthesis of o-cyanobenzamide from acetic anhydride and phthalimide. The physical and chemical properties of phthalocyanines vary depending on whether they have a metal in their center. The first Cu phthalocyanine blue pigment was produced in 1935. Today, it is widely used in applications, such as printing inks, paints, and coatings, due to its bright, clean

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shades and excellent weather-fastness and lightfastness. It is also an effective colorant for painting various surfaces and coloring plastics or polymers, including low-density polyethylene, high-density polyethylene, polypropylene, polyvinyl chloride, and polystyrene [15]. Moreover, there is no alternative to Pigment Blue 15 (PB15); potential substitutes do not have the same colour brilliance or they have greyish tones when blended with white pigments.

The Food and Drug Administration (FDA) released the Inventory of Food Contact Substances Listed in Code of Federal Regulations (CFR) 21 database. This database contains an inventory of substances authorized in Title 21 of the 21 CFR for uses in contact with foods [16]. Phthalocyanine blue, listed in 21 CFR178.3297, is under the category of Food Contact Substances [17]. According to Sec. 178.3297 Colorants for polymers, phthalocyanine blue can be used in the aquatic food packaging materials. So, this pigment is allowed to be used in materials that come into contact with aquatic food as a colorant for polymers intended for use in processing, packaging, and transporting food, but subject to specific provisions [16, 17]. According to the regulation, there is a limited amount, which should not exceed the minimum required for the intended color effect. The pigment is permitted for I, II, IV-B, VI-A, VII-B, and VIII food type categories, which include aqueous, acidic, and fatty foods. Table 1 of 21 CFR 176.170 provides information on the types of food [17]. Type I covers nonacid, aqueous products; that may contain salt or sugar or both, and include oil-in-water emulsions of low- or high-fat content. Type II covers acid, aqueous products; that may contain salt or sugar or both, and include oil-in-water emulsions of low- or high-fat content. Type IV-B: Low-moisture fats and oils. Type VIII covers aqueous, acidic products containing free or combined oil. So this colorant is allowed under conditions of use B through H. These conditions relate to the temperature and duration of contact with food are stated as: B: Refrigerated storage; C: Frozen storage; D: Room temperature storage, with no thermal treatment in the container. E: Room temperature storage with thermal treatment in the container; F: High-temperature, above 121°C, heat-sterilized; G: Aseptic processing and packaging. H: Hot-filled or pasteurized above 66°C. For aquatic food products, considered under food type I (nonacid, aqueous products), the package colored with phthalocyanine blue must comply with the conditions of use that correspond to the intended storage and handling. For instance, if the aquatic food is to be stored refrigerated (condition of use B) or frozen (condition of use C), its in-package must comply with those conditions. According to the regulation quantity of color additive should not exceed 0.5% of the material weight [16]. For phthalocyanine blue usage in seafood packages, the regulation emphasizes the minimum quantity to obtain the desired color without specifying a particular percentage. This is to ensure that the colorant is applied safely without penetrating the food package in high amounts. Excessive amounts could migrate into food, raising safety concerns.

The presence of Cu-Phthalocyanine in paper and plastic products has been previously studied [18]. Cu-Phthalocyanine is subject to regulations, including (EC) No 1935/2004, Art. 3, Risk Assessment and Commission Regulation (EU) No 10/2011, have been left to manufacturer/supplier responsibility. Self-assessment should be done by the manufacturer/supplier according to Art. 19 10/2011 and Art.31935/2004, concerning especially the purity requirements on phthalocyanine blue [18]. The aquatic food packaging industry must ensure safe use and regulatory acceptance. In the US, the food contact notification process requires industry to provide sufficient scientific information to demonstrate that the additives employed are safe for their intended use. According to the EU Regulation (EU) No 10/2011, the total quantity of substances migrating into food simulants is limited to 10 mg/dm^2 (= 100 $\mu g/cm^2$) per food contact surface area [18].

Cu-phthalocyanine is unlikely to diffuse out into polar solvents. According to the study by Zhang et al. [19] no Cu release was detected in the polypropylene plates, and eventually, no released pigment nanoparticles were found. So even at 5% w/w pigment concentrations of Cu-phthalocyanine, no Cu release was detected. This could be attributed to its hydrophobicity, which leads to hydrophobic interactions with the polymer [19]. In the same study, the specific grade of Cu-phthalocyanine is designed for food contact. When pigment concentration increased to 5% (w/w), a deep blue color occurred, but a concentration of 0.5 % would be enough to obtain a blue color, which is more appropriate for the materials that are available on the market [19].

1.2. Gelatin Films for Aquatic Food Packaging

Gelatin is derived from collagen and is a natural biopolymer with good film-forming, biodegradability, and good barrier properties, making it an environmentally friendly alternative to plastics in the food packaging industry [20]. Therefore, there is a growing interest in the production of gelatin films. Due to its low production cost on a large scale and good film-forming properties, it is a potential candidate. Plasticizers can be added to improve the flexibility, extensibility, and dispensability of the gelatin films. Since glycerol reduces inter-chain interactions and modulates the macroscopic functional properties, it has been used plasticizer in gelatin films [21] [22]. It should be noted that the mechanical properties and flexibility of gelatin-

based films may depend on glycerol content [23].

Since Türkiye still imports these blue pigments, in parallel with the development and growing industry, the need for these pigments in Türkiye is increasing day by day. The only phthalocyanine that has commercial importance as a pigment is Cu phthalocyanine. It is the most commercially important phthalocyanine, code-numbered PB15. PB15 Cu phthalocyanines are widely used in printing inks, packaging, paper, and plastics coloring. Since gelatin films are good capping mediators for metallic ions, they are ideal for Cu phthalocyanine capping [24]. Also, it has been reported that Cu-phthalocyanine films can also be used for gas sensing functions, which shows their possibility for intelligent packaging functions [25, 26]. Therefore, this study examined the use of synthesized Cu phthalocyanines in two different gelatin-based films for aquatic food packaging purposes.

2. Material and Method

2.1. Material

The commercially available blue pigment, code PB15:1, was supplied by BASF (Germany). The samples coded PD1 and PD2 we synthesized in our study, were obtained as a result of R&D work. The samples we synthesized in our laboratory and a commercially purchased sample were used as sample material. Bovin skin gelatin Bloom: 200-220, Mesh: 30, Lot Number: K309035 was obtained from the Gerede Gelatin company (Bolu). Acetic acid (Glacial 100%) was purchased from Merck (Germany). Glycerol (99.5%, CAS 56-81-5) in liquid form and distilled water were also used for the experiments.

2.2. Method

2.2.1. Production and Analysis of Cu-Phthalocyanine Pigments

Ash is a residue formed by the oxides of inorganic substances left over as a result of the burning of organic substances. Ash content determinations are made to determine the inorganic substance content of products, especially those containing organic matter in their structure. Ash determination is carried out in a crucible brought to a fixed weight at 600 °C for 45 minutes (Nabertherm 30-3000 °C muffle furnace) for 2 hours, and then the crucible is weighed and the ash content is calculated. Pigments PD1 and PD2 obtained as a result of pigmentation were characterized using different spectroscopic methods and elemental analysis according to the literature [27]. Two produced compounds with code numbers PD1 and PD2 were synthesized. HPLC (Zivak®) and Zivak® Tandem Gold Triple quadrupole mass spectrometer, having a Phenomenex Synergi 4u Max-RP 80A column (150 x 2.0 mm i.d., 4u m particle size) and Agilent 7700 series Inductively coupled plasma mass spectrometry (ICP-MS) were used for instrumental analyses. FTIR data were obtained with a Perkin Elmer Spectrophotometer (Lambda 25, Waltham, MA) equipped with an ATR device at 4/cm resolution. Samples were examined in the transmission mode in the wavenumber range of 4000–650 cm^{-1}.

2.2.2. Gelatin Film Production and Analysis

For gelatin film production, at first, 30% wt gelatin and 10% glycerol (GL10), and 5% glycerol (GL5) as a plasticizer were dissolved in a 4:1 acetic acid: distilled water mixture, by stirring at 50 °C for half an hour (Table 1). Then, the synthesized selected PD1 was added at 0.5% to the film-forming solution. Since a concentration of 0.5wt% is sufficient to impart a full blue color that is more typical for materials available on the market [19].

Table 1: Film compositions.

Sample	Gelatin (%)	Glycerol (%)	Solvent (%)	PD1 (%)
GL10	30	10	59.5	0.5
GL5	30	5	64.5	0.5

After the homogenization on a magnetic stirrer, the mixture was poured into glass Petri dishes (10x10 cm) and dried for two days at room temperature. Then, the obtained films were removed from the Petri dish and stored before the color, mechanical, and compression tests. The thicknesses of the GL10 and GL5 films were measured as 300 ± 10 µm and 370 ± 10 µm, respectively, using a digital compass.

L lightness (0-100 black-white), *a* (redness + and greenness-), *b* (yellowness +, and blueness −) of gelatin films were measured using Fru® Precise Color Reader (Model: WR-10; S/N: 1000200469; Shenzhen Wave Optoelectronics Technology Co., Ltd.) equipped with an 8-mm caliber. Hue angle (tone or hue, color saturation) and chroma (Chroma, color intensity) were calculated using the equations below [28]:

$$\text{Hue angle} = \arctan(b/a)$$

$$\text{Chroma} = (a^2 + b^2)^{1/2}$$

The mechanical properties were calculated by using Texture Analyser (Lamy Rheology, TX-700) with the modified method of He et al. [29]. A rectangular piece of the film sample (0.3mm×2mm) was pulled with a crosshead speed of 0.1 mm/s at room temperature. Initial distance was fixed at 20 mm between the film ends. Three specimens of each film were analyzed, and the average values of

mechanical property parameters were reported with standard deviations.

The solid-state viscoelastic behavior of the samples was evaluated by creep tests conducted on a dynamic mechanical analyzer (SII Nanotechnology, ExStar DMS 6100). In creep tests, a constant stress of 0.5 MPa was instantaneously applied to the specimen at room temperature, and the resulting time-dependent creep strain was monitored for 30 min. Then, the stress was removed, and the recovery response was also monitored for 30 min.

Brookfield CT3 1000 V.19 (Brookfield Engineering Laboratories, Middleboro, USA) was utilized to determine deformation rates using a modified single compression test. Accessories Rotary Base Table (TA-RT-KIT), TA44 Cylinder probe (4 mm diameter, stainless steel) was used. Data rate was 10 points/sec. Deformation tests at 25, 50, 75, and 100% target values were utilized. Deformation rates were as follows: 25%: 0.31 mm, 50%: 0.65 mm, 75%:1.23 mm, 100%:1.72 mm. Differences at various deformations in terms of hardness (Newton), springiness (mm), cohesiveness, gumminess (Newton), chewiness (mj), load at target (Newton), and average peak load (Newton) were revealed at room temperature. Parameters were derived from force-deformation curves and interpreted in the context of thin film behavior.

2.2.3. Statistical Analysis

Data were presented as mean value ± standard deviation for the compression test and color results. The data were analyzed by one-way analysis of variance (ANOVA) using the Tukey test to determine if there were significant differences in the mean values.

3. Results and Discussion

3.1. Chemical Analysis of Pigments

Using ash determination and ICP analyses, the amount of Cu in the existing compound was determined and compared with that of the commercial one (control; Cu 11.99%; Ash 10.8%). Therefore, after several trials, it was determined that the closest ones to the commercial sample were the PD1 (Cu: 11.94%, Ash 23.8%) and PD2 (Cu: 12.41%, Ash 12.3%) coded trials in terms of both the amount of Cu and the FTIR result for the synthesis. The most appropriate method was decided by obtaining the purity value data clearly and performing cross-validation. We have included the HPLC purity data in our report and made informed decisions based on cross-validation.

HPLC analyses were performed on all samples to remove impurities and detect interferences. Upon examining the results, the purity of PD2 is nearly identical to that of the commercial sample (Figure 1a). Retention time indicates how long a compound stays in the column before being detected. The height of the peaks represents the intensity and the concentration of the compounds. Closer peak retention times and similar symmetrical shapes show that compounds are similar in terms of concentration and molecular structure. Baseline instabilities were observed in both samples between 2-2.7 and 3.2-3.4 minutes.

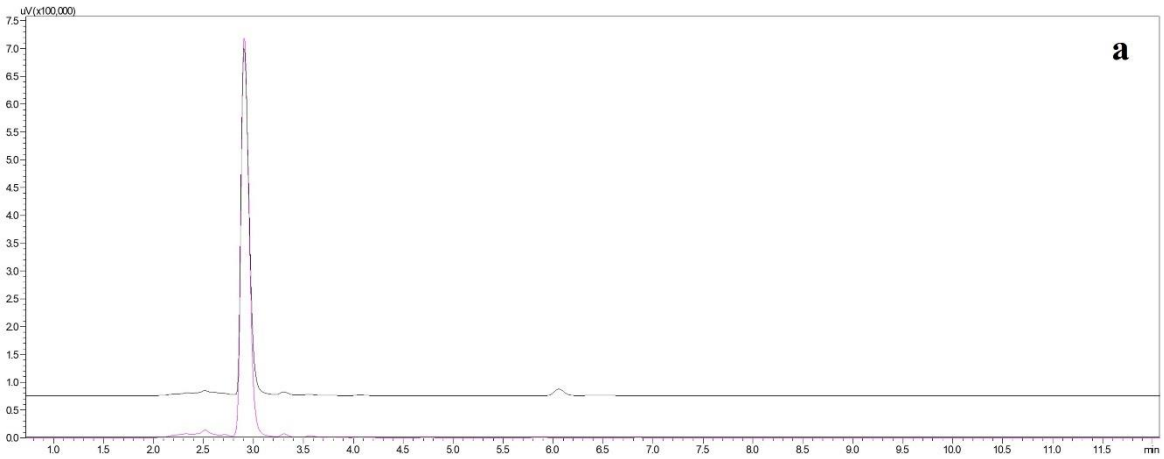

Figure 1. HPLC results of PD2 (pink) and PB 15 control (black) samples (a). HPLC results of PD1 (pink) and PB 15 control (black) samples (b)

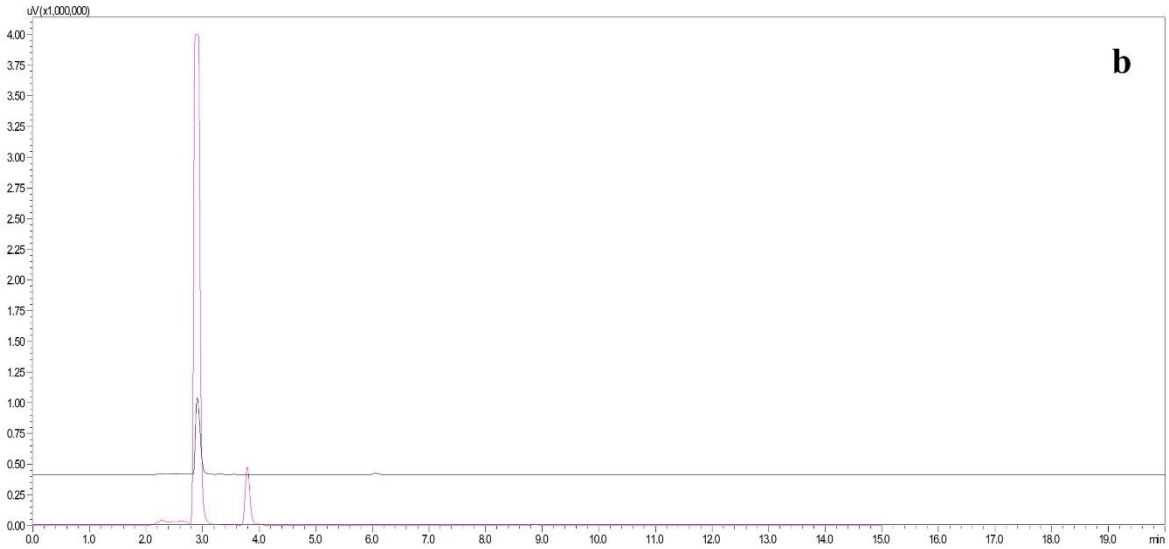

Figure 1. (Cont.) HPLC results of PD2 (pink) and PB 15 control (black) samples (a). HPLC results of PD1 (pink) and PB 15 control (black) samples (b)

In sample PD1, although the retention times of the first peak were similar, impurities were detected. Peak intensities were higher, and the peak shapes were different. Additionally, a second peak was detected around minute 3.7. While impurity removal efforts on PD1 are ongoing, this is the closest synthesized sample to our commercial sample code PB15:1.

3.2. FTIR Analysis Results

FTIR analysis is one of the most crucial tests to confirm the synthesis of the compound and one of the widely used spectroscopic methods for characterizing the chemical structures of molecules Yılmaz and Bayıl [30]. FTIR analysis plays an important role in the chemical characterization of components and is a simple method that provides fast results compared to traditional analytical methods. We have proved that the synthesis took place by comparing FTIR results with commercial PB15 pigment. Compounds were synthesized, and the existing interferences were detected in the spectra. The bands of the pigments and the commercially purchased PB15 code pigment are seen in Figure 2. The pink bands are commercial, black and gray ones are the bands of the newly synthesized samples.

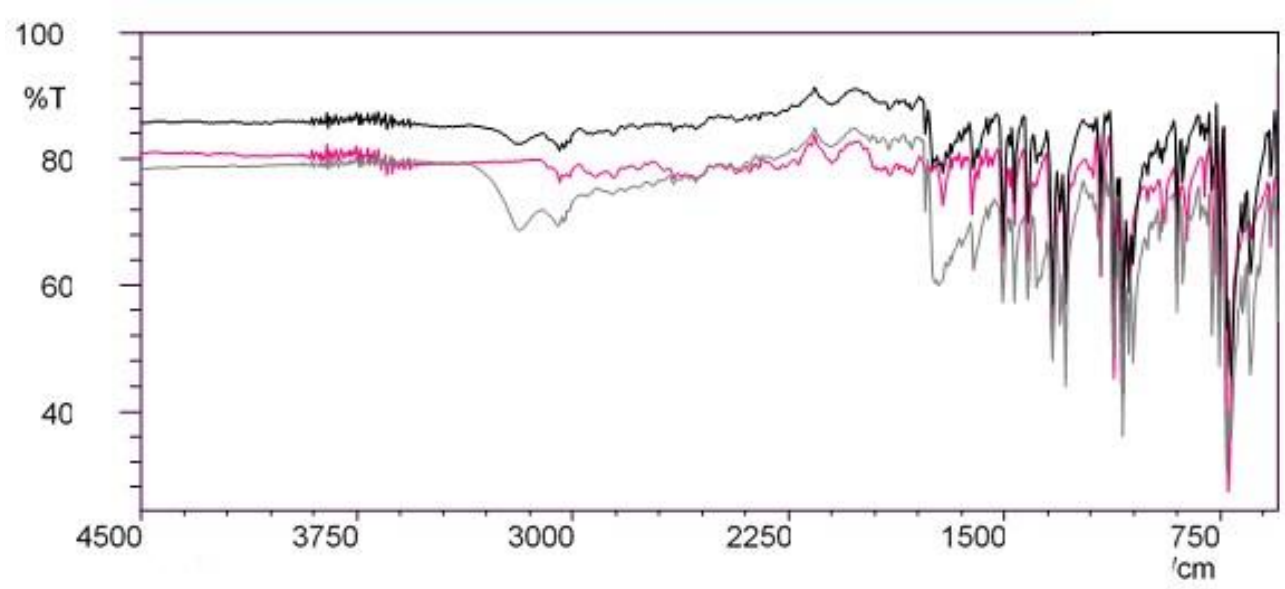

Figure 2. FTIR spectrums of PB15 (pink), PD1 (black) and PD2 (gray) pigments

C-H bending vibrations in the range of 750-850 cm^{-1}, C-N vibrations in the range of 1100-1300 cm^{-1}, C=C and C=N stretching vibrations in the range of 1400-1600 cm^{-1}, and N-H bending vibrations in the range of 3200-3400 cm^{-1} were observed. It was also observed that the PD2 sample had higher stretching vibrations than the PD1 sample. Overall, around 2900, 2000 cm^{-1}, 1450 cm^{-1}, similar bands were seen in all three samples' spectra. It can be concluded that PD1 sample peak stretchings were closer to the commercial sample.

3.3. Color of the Gelatin-Based Films

According to the literature, L values are relatively high for neat gelatin films. For instance, it has been previously stated that gelatin films incorporated with 10% chitosan and glycerol had an L value of 96.50 ± 0.50 [24]. However, it would be expected that colorants reduce the L value. For instance, in a study by Cetinkaya et al. [31] addition of red colorant extract reduced the L value from 93 to 79. In the current study, for the GL10 sample, L was found as 27.91 ± 0.25, showing a strong effect of colorant on the L value (Table 2). Since a higher value represents redness, it should be close to 0. Our results were 2.9 and 3.36 for the GL10 and GL5, respectively. According to the color scale, the b value must be lower than 0 for the blue color. In both samples, it was lower than 0, supporting each other that the color is blue. Results showed that glycerol didn't significantly affect the color properties of the films, indicating high color stability ($p>0.05$).

Table 2. L, a, b, Hue angle, and chroma value parameters of the gelatin-based films

Parameter	GL10	GL5
L	27.91 ± 0.25[a]	29.16 ± 1.75[a]
a	2.9 ± 0.32[a]	3.36 ± 1.05[a]
b	-0.94 ± 0.25[a]	-0.66 ± 1.13[a]
Hue Angle	342.12 ± 3.28[a]	353.19 ± 18.92[a]
Chroma Value	3.05± 0.37[a]	3.53± 1.16[a]

[(a)]Means values with the same superscripts within the same line are not significantly different ($p > 0.05$).

A Hue angle value lower than zero can be adjusted by adding 360 degrees. This adjustment brings the value within the standard range of 0 to 360 degrees, which is commonly used in color measurements [32]. In a study by Francis [33], for blueberries, blue Hue was found as -6.8, which then converted to 353.2, identified in quadrant 4 (270-360). In our study, when these values, -17.88 and -6.81, were adjusted, the results were found as 342 and 353, respectively. Hue angle >280° and <360 illustrated with a blue hue and b<0 [34]. So, our results prove the blue color of the samples. Similarly, Anter [35] found the Hue angle of the blue color as -2.

Chroma refers to the strength or saturation of a color. Chroma may describe the color intensity or purity. Colors with low chroma may be more dull or muted. Chroma values were 3.05 and 3.53 for GL10 and GL5 samples, respectively. A chroma value less than 5 generally indicates a muted or less vibrant shade of blue. When using phycocyanin blue at 1%, paper, plastic, polylactic acid, polyamide, and polyurethane-based materials also showed a deep blue color [18].

According to all color parameters, both samples had high stability. Although differences were insignificant, the GL10 sample showed better blue color results.

3.4. Mechanical Properties of Films

Figure 3 presents representative tensile test photographs of a specimen at various strain steps, including the breaking point. As can be seen, films showed high extensibility under tensile stress, making them suitable for flexible packaging applications.

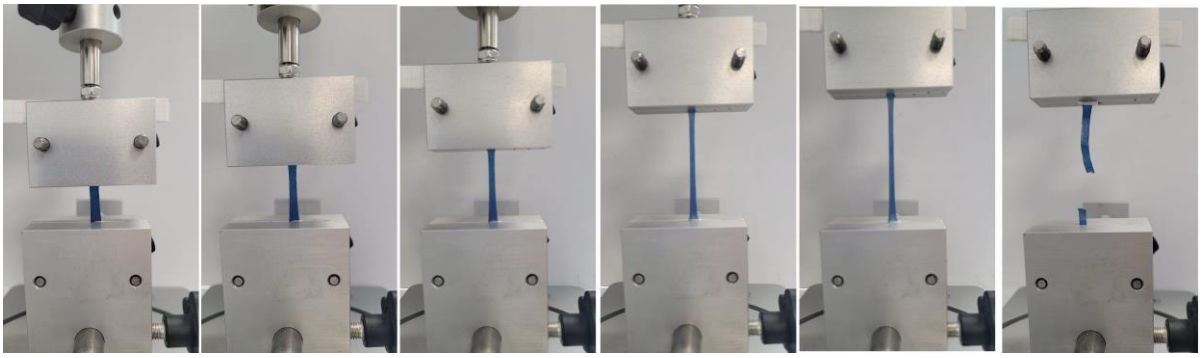

Figure 3. Representative photographs of the tensile test

Figure 4 illustrates the typical stress–strain curves of samples. The tensile test results showed that GL5 and GL10 exhibited distinct mechanical responses, particularly in terms of modulus and elongation at break (ε_b). As evidenced by the stress–strain curves, neither sample did not display a yielding behavior, which was also confirmed by the fact that no necking formation occurred in the test photograph. The mechanical properties of the samples were evaluated using several parameters obtained from the stress-strain curves, as listed in Table 3.

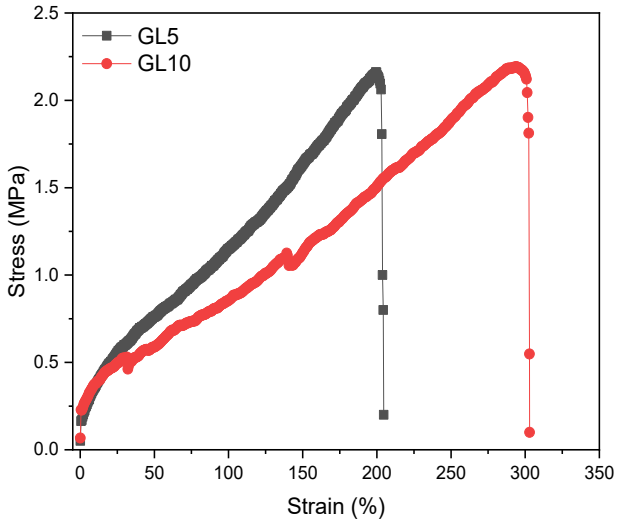

Figure 4. Stress-strain curves of samples

GL5 exhibited a higher Young's modulus (E_a) compared to GL10. In addition to the Young's modulus (also called tangential modulus), which is determined from the initial slope of the stress–strain curve, the elasticity of the samples was also evaluated in terms of the secant modulus (E), defined as the slope from a selected point on the curve to the origin. This approach is particularly relevant for soft and amorphous specimens that do not exhibit necking, since their elasticity is more appropriately characterized by the stress resistance or load-bearing capacity at relatively higher strains rather than by the initial loading region, where relaxation effects are more pronounced. Considering the strain at break values of the samples, a strain of 100% was selected as the comparative point in this study, and the $E_{100\%}$ values were calculated accordingly as the secant modulus. It is seen that GL5 also exhibited a higher secant modulus compared to GL10.

Table 3. Mechanical properties of samples

Sample	E_a (MPa)	$E_{100\%}$* (MPa)	TS (MPa)	ε_b (%)
GL5	1.62 ± 0.3	1.23 ± 0.08	2.25 ± 0.09	198.5 ± 1.5
GL10	1.05 ± 0.06	0.85 ± 0.03	2.05 ± 0.17	305.3 ± 8.8

*$E_{100\%}$: %100 secant modulus
TS: tensile strength

Suderman, Isa, and Sarbon [36] indicated that 2.67:1 bovine gelatin: glycerol films prepared with distilled water show a peak load in the range of 2.97 MPa. The difference could be attributed to the presence of acetic acid or gelatine: glycerol ratio. GL10 exhibited higher elongation at break and lower modulus values compared to GL5, while the tensile strengths of the two samples were relatively close, with GL5 being slightly higher. These differences can be attributed to the plasticizing effect of glycerol. Overall, these findings indicate that GL10 was softer than GL5, making it more ideal for flexible packaging, which is selected for compression tests.

3.5. Solid-state Viscoelastic Properties of Films

Figure 5(a) shows the creep and recovery curves of the samples. In creep curves, both samples exhibited an instantaneous strain upon loading, which was subsequently followed by a time-dependent creep deformation. It was found that GL10 exhibited higher strain values than GL5 in both the instantaneous deformation region and the total strain measured during the 30-minute test period.

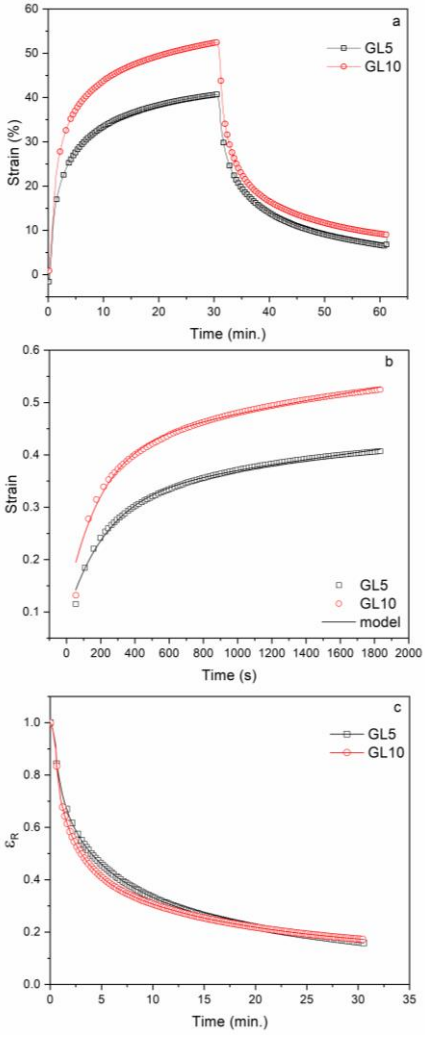

Figure 5. (a) Creep and recovery, (b) Burger model fit, and (c) relative recovery curves of samples

In Figure 5(b), the creep response of the samples is modeled with the four-element Burger equation. This viscoelastic representation combines the Maxwell and Kelvin-Voigt systems and is regarded as one of the most widely applied mathematical approaches to describe the viscoelastic behavior of thermoplastics, elastomers, and composites [37–40]. This model has also been successfully applied to various polymeric systems, including biopolymers such as gelatin and starch [41, 42]. The mathematical expression of the Burger model is given as;

$$\varepsilon(t) = \frac{\sigma}{E_M} + \frac{\sigma}{E_K}\left[1 - \exp\left(-\frac{E_K}{\eta_K}\right)\right] + \frac{\sigma t}{\eta_M}$$

where ε(t) is the strain as a function of time, σ represents the applied stress, E_M and ηM correspond to the elastic and viscous parameters of the Maxwell element. Similarly, E_K and η_K indicate the elastic and viscous components of the Kelvin element. Comprehensive mathematical and physical descriptions of the Burger model are provided in the literature [43]. The creep behavior of the samples was successfully fitted using the Burger model, and the corresponding parameters are presented in Table 4.

Table 4. Burger model parameters of samples

Sample	E_M	E_K	η_M	η_K
	(MPa)	(MPa)	(MPa.s)	(MPa.s)
GL5	5.5	2.1	11032	490.0
GL10	3.9	1.6	8566	348.0

It was found that all viscoelastic parameters of GL5 were higher than GL10. The parameter E_M is commonly regarded as the elastic modulus, corresponding to the elastic or Young's modulus of a viscoelastic material. The lower E_M value of GL10 (3.9 MPa) compared to GL5 (5.5 MPa) indicates that GL10 is softer and more flexible than GL5. These findings are consistent with the tensile test results, where GL10 demonstrated higher elongation at break and lower modulus values, confirming the plasticizing effect of glycerol.

Figure 5(c) shows the recovery curves of samples normalized with the final strain of the creep deformation. The results indicate that there is no significant difference in the recovery behavior of the samples. This demonstrates that the addition of glycerol increases flexibility without affecting the material's elastic recovery capacity. This behavior can be attributed to the relaxation behavior of samples, mainly dependent on the polymer phase rather than the amount of plasticizer.

3.6. Compression Tests of the Selected Gelatin Film

Compression tests are important when describing the qualified characteristics of films [44]. It was found that there is a relationship between mechanical and textural properties and glycerol concentration of gelatin-based films [45]. As can be seen from Figure 6 and Table 5, the selected sample GL10 has the highest load at 100% deformation rate, at the maximum point of distance, 1.72 mm. The hardness values for similar gelatin films were reported to have values ranging from approximately 2 to 5 Newton previously [46, 47]. Our results were in accordance, since the first cycle hardness values were between 2.32-6.71 Newton. Springiness is the film's ability to return to its original shape after being compressed, which may be an important parameter for film packages that need flexibility and resilience.

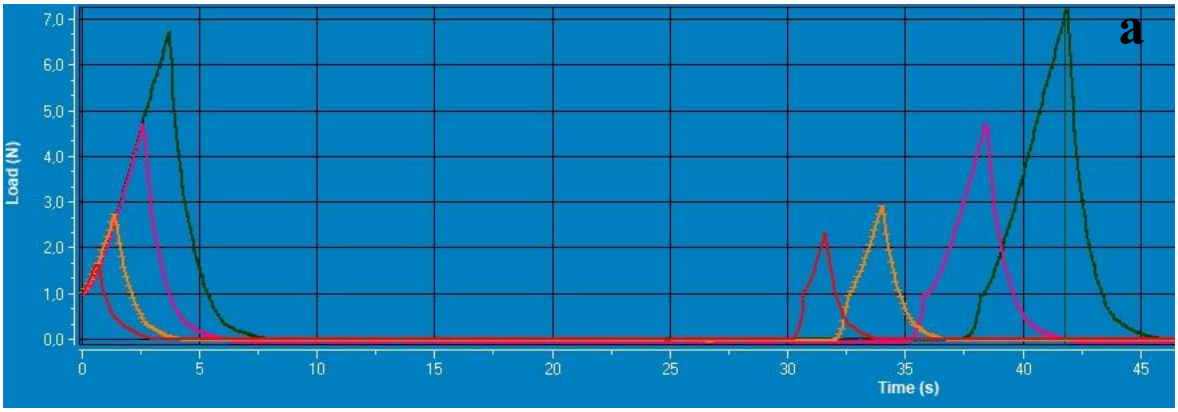

Figure 6. Load changes over time (a) and required force with deformation of GL10 film at 25 (red), 50 (orange), 75 (pink), and 100% (green) deformations (b)

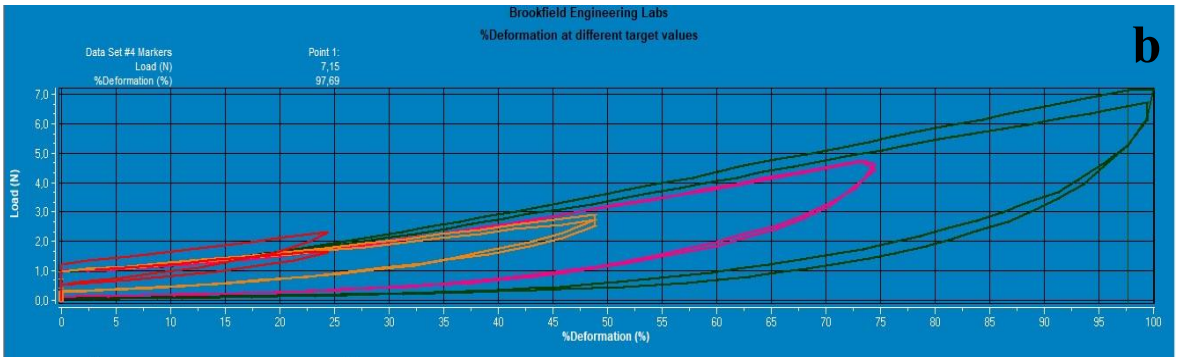

Figure 6. (Cont.) Load changes over time (a) and required force with deformation of GL10 film at 25 (red), 50 (orange), 75 (pink), and 100% (green) deformations (b)

Yap et al. [48] reported that the cohesiveness value for gelatin films with 10% glycerol was 0.66, confirming that our results were consistent.

Gumminess is another important parameter for applications when the film requires maintaining a certain level of chewiness or resilience. Gumminess is correlated with hardness; therefore, similar to hardness, its value increased at the highest deformation rate. However, Porayanee et al. [44] observed higher gumminess values in gelatin films, compared to our results. The load at target, a force measured in Newton, is required to compress the sample to a predetermined distance or percentage of its original height. The load at the targeted value was also increased with increasing hardness values. The average peak load is the maximum force that the film can withstand during a test before deformation.

Table 5. Compression test parameters of the GL10 film at 25, 50, 75, 100% deformations

	Deformation Rate			
Parameter	**25**	**50**	**75**	**100**
Hardness Cycle 1 (N)	2.32	2.74	4.71	6.71
Springness (mm)	0.41	0.62	1.24	1.65
Cohesiveness	-	1.1	0.98	1.15
Gumminess (N)	-	3.05	4.59	7.7
Chewiness (mj)	-	1.89	5.7	12.7
Load at target (N)	1.64	2.74	4.45	6.13
Average peak load (N)	1.98	2.83	4.7	6.95

4. Conclusions

While designing packages' visual appearance, it's necessary to ensure that they successfully deliver the desired message and are compatible with consumer expectations. Blue is perceived as a color that represents honesty and truth, which may affect the perception of consumers. According to 21 CFR §178.3297, it is permitted for use in coloring polymers that are intended for use in contact with aquatic food, under certain conditions. The regulation specifies that the colorant can be used when it is used in amounts not to exceed the minimum required to produce the intended color. For this purpose, commercial PB15 properties are compared with synthesized samples. HPLC peaks in the synthesized samples matched those in the commercial (control) sample. Cu content in the PD1 (11.94%) sample compound was closer to the commercial sample (11.98%). After PD1 addition to gelatin solution and film manufacturing, Hue angle values between 280°-360, b values less than 0, and Chroma less than 5, resulted in a dull blue color of the films. Color parameters revealed that the 30% gelatin and 0.5% phthalocyanine blue pigment-containing film, GL10, had higher stability. Moreover, it showed higher ε_b, making it more flexible, which is often preferred in the meat industry because of its versatility, cost-effectiveness, and barrier properties. Therefore selected GL10 film compression test showed up to 6.95 N peak load at 100% deformation rate. It was concluded that phthalocyanine blue pigment at 0.5% can be used as a colorant in aquatic food packaging materials, provided that all requirements are met. In the future, the minimum effective concentration required for adequate coloring must be determined, while ensuring compliance with safety standards, such as migration rate.

Declaration of Ethical Standards

The author of this article declares that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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