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ORIGINAL ARTICLE

Coloration Technology

Development of polycaprolactone-based electrospun pH-sensitive sensors as instant colorimetric indicators for food packaging

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Abstract

In the present study, polycaprolactone/polyethylene glycol (PCL/PEG) electrospun nanofibres with different anthocyanin (1%, 2%, 3%, and 5%) were fabricated for the instant measurement of pH, especially for applications—such as food freshness detection—where quick response is required. The solution, surface, chemical, thermal, wettability, mechanical, and release properties of the samples were evaluated by viscosity measurements, scanning electron microscopy (SEM), Fourier-transform infrared (FTIR), contact angle measurements, and tensile tests, respectively. The colorimetric analyses were also investigated against the solutions at different pH values and bacterial solutions. Finally, the on-site performance of the sensor was evaluated. Anthocyanin addition initially lowered the solution viscosity, resulting in thinner fibres with a diameter of 288 nm. The diameters were increased up to 395 nm with the increasing anthocyanin. Anthocyanin addition enhanced the wettability and the mechanical properties, and the contact angles decreased to 43°. The highest modulus was observed for 1% anthocyanin, with a value of 6.162. The release experiments revealed that the anthocyanin-loaded samples released a large amount of anthocyanin (between ~12% and 38%) in the first 15 s. The colorimetric analyses showed that PCL/PEG nanofibre mats with 2% and 3% anthocyanin concentrations were the most capable pH-sensitive sensors for detecting pH changes from 2 to 8. As a result, it can be concluded that 3% anthocyanin is the threshold value for the production of the anthocyanin-loaded nanofibre mats, and these structures are promising for the instant detection of pH proved by the on-site application.

1 | INTRODUCTION

The colour change can be a vital signal to prevent the human from danger when an environmental change occurs. Stimuli, such as pH, temperature, light, electrical or magnetic fields, and biological changes can trigger environmental changes. Detection and monitoring of pH are the most studied subject among these triggers.[1,2]

Fast, accurate, sensitive, and reversible colour changes are expected in such changes. To achieve them, porous and permeable structures are needed. Nanofibres offer suitable surfaces with their high surface area-to-volume ratio, small

pore sizes, high porosity, and high mechanical properties.[3,4] These characteristics provide enhanced sensor sensitivity and response time. Moreover, pH-responsive sensors can be developed by adding dyes, such as alizarin, bromocresol green, bromocresol purple, thymol blue, and nitrazine yellow, to the nanofibres.[5–7] These sensors can be used in many application areas, including monitoring food freshness, wound dressing, water treatment, acidic gas detection, etc.[7–10] For instance, Kalisz et al, investigated the potential of electrospun polyvinyl chloride (PVC) and polycaprolactone (PCL) with 10,12-tricosadiynoic acid or 10,12-pentacosadiynoic acid as colorimetric and fluorimetric pH sensors. The PVC/PCL mixture was chosen to benefit from PCL's ability to plasticise PVC and avoid the application of a liquid plasticiser. The prepared sensors were studied in two readout modes: colorimetric using a smartphone camera and fluorimetric one. Their experimental results demonstrated that both readout modes could be successfully used for pH sensing with proposed nanofibrous mats in the range of pH close to the physiological pH range.[11] In another study, Park et al produced a textile-based colorimetric sensor for acidic gas detection using rhodamine dye with improved thermal properties. They investigated the sensitivity, durability, and reversibility of the fabricated textile sensors and showed that the sensor they fabricated could be a promising candidate for practical sensor applications.[9]

Another application area of nanofibre mats with pH sensing materials is health monitoring, especially pH-responsive electrospun wound dressings. To fabricate electrospun nanofibrous wound dressings, synthetic halochromic pH-sensing dyes can be used. However, these dyes can be toxic or allergic. Therefore, natural halochromic pH-sensing dyes derived from plants of coloured fruits or vegetables, such as anthocyanins, are good alternatives for such applications.[12] Anthocyanins have excellent antioxidant, antimicrobial, and pH-sensitive properties.[13] Moreover, they are preferable for pH-sensing applications due to their easy integration into the nanofibre structure. Up to now, numerous studies have been performed on their usage as wound healing monitoring.[14–18] The studies showed that the anthocyanin-loaded nanofibre mats could sense pH changes and be successfully used as a wound dressing material.

Among many applications of anthocyanins as pH sensors, one of the most studied applications is their usage as smart/intelligent packaging materials. Selection of carrier polymer is a key point for such applications. These sensors can be produced from a wide range of polymers, such as chitosan, cellulose acetate, polyvinyl alcohol, polyurethane, polyacrylonitrile, and so on.[6,7,19–21] In practical applications of anthocyanin-loaded nanofibre mats, leakage of water-soluble anthocyanins from water-soluble polymers is a problem encountered. Especially in food packaging applications, the usage of water-soluble polymer causes the destruction of the structural integrity of the sensor due to the water vapour caused by the temperature difference between the inside and outside of the refrigerator. In this case, using polymers with highly hydrophobic characteristics as a matrix material can be a good alternative. However, the higher hydrophobicity of the sensor can lower the reaction sensitivity of the sensor, whereas the hydrophilic polymers can improve sensor stability. Therefore, the key point for hydrophobic sensors is improving the sensor reaction sensitivity.[22]

Among many polymers, PCL stands out due to its non-toxicity, biodegradability, slow degradation, easy electro-spinnability, and good mechanical properties.[23] However, PCL is a highly hydrophobic polymer. Although high hydrophobic polymers can be used to improve the self-integrity of the sensors in pH-sensing applications, this may also limit their pH response. In order to overcome this restriction and achieve a higher response, the hydrophilicity of PCL can be enhanced by adding a leachable polymer such as polyethylene glycol (PEG),[24] polyethylene oxide (PEO),[25] polyvinyl alcohol (PVA),[26] and polyvinylpyrrolidone (PVP),[27] etc.

In recent years, many studies have been published on producing PCL-based halochromic sensors. Liu et al aimed to design a new colorimetric indicator electrospun sensor with high sensitivity and stability by using PCL and anthocyanin as the polymer matrix and halochromic component, respectively. One of their aims was to improve the hydrophobic properties of the sensor by mixing PCL and anthocyanin. The PCL nanofibre layer was intended to act as a protective layer against harsh environments as strong hydrophobic with high contact angle values. The results showed that the indicator exhibited high sensitivity to pH solutions for colour change and ammonia gas reversibility cycling having potential as a smart packaging material.[28] Zou et al developed pH-responsive extract-loaded PCL-based nanofibre mats with antibacterial properties for active and intelligent food packaging. In their study, shikonin and chitosan were used as pH-sensitive and hydrophilic components, respectively. They indicated that the surfaces with shikonin were promising for monitoring the shrimp freshness by changing colour.[29] Da Silva et al fabricated açaí-loaded fibres by electrospinning as pH sensors with potential applications in the food industry by using PCL and PEO as the polymers. They concluded the açaí extract-loaded samples responded to pH changes.[30] Terra et al investigated the colour variation properties of PCL/PEO nanofibres with phycocyanin at different pH over time. The samples showed an increasing colorimetric profile in 20 h of exposure to buffer solutions from pH 2 to 7.[31] Terra et al developed electrospun PCL/PEO pH indicators containing phycocyanin for monitoring food quality. They concluded that 2% phycocyanin-loaded PCL/PEO

nanofibres were found as a promising indicator in food packaging applications.[32] Jovanska et al also produced PCL/PEO nanofibres as pH sensors for food monitoring by loading *Hibiscus rosa sinensis* extract and silver nanoparticles. They also studied the suitability of PCL and PEO as carriers. Their study revealed that these polymers were desirable carriers, and the double network polymers adjusted the hydrophobicity and hydrophilicity of fibres that interacted with liquid samples appropriately. One of their study's main findings was that they retained most pigments in the structure during most pH monitoring situations.[25]

Considering the issues explained earlier, the present study has focused on developing anthocyanin-loaded PCL nanofibre mats for pH-sensing applications, especially instant pH measurement. One of the most distinctive points of this study is the low molecular weight PEG usage as the leachable polymer. A problem faced by using a leachable polymer may be the leakage of the pH-sensing material. Some studies in the literature focused on preventing halochromic dye leakage from the nanofibres for repetitive usage.[33,34] The aim of this study is to produce a non-reversible sensor for single-use, especially for instant pH measurement. Hence, the quick leakage of the anthocyanin, which means the quick response of the sensor, is crucial. In the literature, it was shown that PEG releases faster than PEO due to the small molecule size of PEG.[35] This release behaviour can also be favourable for instant pH detection. PEG's quick removal from the structure when interacting with the liquid may result in a quick response to the pH changes. Apart from this, the maximum anthocyanin ratio in the nanofibre and pH changes against antibacterial activity were also determined in the study. At first, the PCL/PEG nanofibre mat without anthocyanin was produced as a reference. Subsequently, anthocyanin with different concentrations (1%, 2%, 3%, and 5% wt, respectively) was put into PCL/PEG solutions. After electrospinning, the surface properties were characterised by scanning electron microscopy (SEM) analyses. The presence of anthocyanin on the surfaces was investigated by energy dispersive spectroscopy (EDS) and Fourier-transform infrared spectroscopy (FTIR) studies. The mechanical properties were determined by the tensile tests. In order to understand the release behaviour of PEG from the nanofibre mats, dye release experiments were conducted and monitored by an ultraviolet-visible (UV-vis) spectrophotometer. The wettability was determined by contact angle measurements. In the CIELab colour space, colour changes were measured against the solutions at different pH and the bacterial solutions for analysing pH response. Consequently, the selected sample with the most appropriate properties was placed on a chicken breast to understand the on-site performance of the sensor.

2 | MATERIALS AND METHODS

2.1 | Materials

In this study, PCL (Mn = 80 kDa, Sigma-Aldrich), PEG (Mw = 10 kDa, Sigma Aldrich), methanol (Merck), and chloroform (Sigma-Aldrich) were used as the polymers and solvents, respectively. A commercially available anthocyanin (E163, Gemma, particle size 70-80 μm) was used as the pH-sensing dyestuff.[36] All chemicals were used without any purification.

2.2 | Methods

2.2.1 | Solution preparation

Firstly, to prepare PCL/PEG solutions, PCL (7%, w/v) was added into the methanol/chloroform mixture (1:3, v/v) and stirred at 35°C until it was completely dissolved. After that, PEG (2%, w/v) was also put in this solution, and the final solution was stirred at 35°C for 30 min. Secondly, anthocyanin was added into the PCL/PEG solutions with a weight of 1%, 2%, 3%, and 5% (w/v) of the solutions, respectively, and the final solution was sonicated for 30 min.

2.2.2 | Solution characterisation

The viscosity of the solutions was measured using a Brookfield (DV-II+ Pro Extra) viscometer at 100 rpm. The pH values of the solutions were evaluated by a Hanna (HI2020-02-edge) pH meter. Besides, in order to understand the pH properties of anthocyanin, 0.1 g of anthocyanin was dissolved in 20 ml of distilled water. Later, pH values of distilled water and anthocyanin-added distilled water were measured. All experiments were performed at 20 ± 2°C.

2.2.3 | Electrospinning process

PCL/PEG and anthocyanin-loaded PCL/PEG solutions were electrospun by an Inovenso electrospinning device shown in Figure 1. The device consisted of a feeding pump, a high-voltage source, and a rotating collector. As seen in Table 1, the electrospinning parameters were chosen as the most suitable parameters that allow nanofibre production. The voltage values were altered accordingly depending on the increasing anthocyanin concentration in the spinning solution. For the sake of brevity, the samples loaded with 1%, 2%, 3%, and 5% anthocyanin were

denoted as PCL/PEG/1%ACN, PCL/PEG/2%ACN, PCL/PEG/3%ACN, and PCL/PEG/5%ACN, respectively.

2.2.4 | Nanofibre characterisation

The surface morphology and the elemental composition of the electrospun nanofibre mats were investigated by SEM-EDS (Carl Zeiss/Gemini 300). Before analyses, the samples were coated with a gold/palladium (Au/Pd) mixture by a Leica/ACE600 high vacuum sputter coater. The average nanofibre diameters were calculated over 50 measurements on SEM images by using ImageJ software.

FTIR analyses were carried out to investigate the anthocyanin presence in the nanofibre mats. The analyses were performed on the surfaces using Thermoscientific/Nicolet i50 Model FTIR in the 600-4000 cm^{-1} wavenumber range, and 32 scans were taken at a resolution of 4 cm^{-1}.

FIGURE 1 Electrospinning device.

Contact angle measurements were performed to understand the interaction between water and the nanofibre mats, defined as surface wettability. The experiments were conducted on a KSV Modular CAM 200 system via the sessile drop technique.

The average thickness values of the nanofibre mats were measured with a micrometre and the tensile tests were performed using a Shimadzu AG-X model universal testing machine with a crosshead speed of 20 mm/min and a gauge length of 20 mm. The average tensile strength and elongation values were calculated over five measurements for each nanofibre mat. The stress-elongation curves were plotted with the measurement values that gave the closest result to the average values.

2.2.5 | Release experiments

The release properties of the anthocyanin-loaded samples were evaluated using Shimadzu UV-1601 Model UV-vis spectrophotometer. Prior to the test, the calibration curve was established by measuring the absorbance of 0.05, 0.1, 0.15, and 0.2 mg/ml aqueous solution of anthocyanin at 282 nm in the 200-600 nm using the spectrophotometer, respectively. Afterwards, the samples were cut into square pieces (1.5 cm × 1.5 cm) and weighed, and put into glass vials containing 2 ml of distilled water. During the experiment, anthocyanin was released from the nanofibre into the water at certain time intervals (15, 30, 45, 60, 120, 180, 240, and 300 s), and water intensity was measured periodically by the spectrophotometer. The experiment was continued by immersing the samples into 2 ml of fresh distilled water each time. The anthocyanin concentrations were calculated using the calibration curve. The cumulative release of anthocyanin was calculated by using Equation (1):

$$\text{Cumulative release}\,(\%) = (W_t/W_c) \times 100 \qquad (1)$$

where, W_t (in milligrams) is the total amount of anthocyanin in the release medium at time t, and W_c (in milligrams) is the total content of anthocyanin loaded. For each sample, the release experiments were performed in triplicates. All experiments were conducted at 20 ± 2°C.

TABLE 1 Electrospinning parameters.

Sample	Flow rate (ml/h)	Distance (cm)	Collector speed (rpm)	Voltage (kV)
PCL/PEG	0.7	15	300	15
PCL/PEG/1%ACN				18
PCL/PEG/2%ACN				18
PCL/PEG/3%ACN				19
PCL/PEG/5%ACN				20

2.2.6 | The pH response and colorimetric analyses

The colour changes and pH responses were measured by a Konica Minolta CMz-3600d spectrophotometer. Spectroscopic analyses were performed while the nanofibre mats were wet. Nanofibre mats were folded four times to prevent light penetration during the analyses. All samples were exposed to buffer solutions with different pH values. The following buffer solutions were used to determine the pH response: formic acid buffer for pH 2, formic acid buffer for pH 4, acetic acid buffer for pH 6, and sodium carbonate buffer for pH 8 and 10, respectively.

International Commission on Illumination (CIE) $L^*a^*b^*$ colour space coordinates were used for observing the colour sensing of anthocyanin-loaded nanofibre mats at different pH conditions. In the CIE colour space, L^* stands for lightness, a^* represents the position ($+a^*$) redness/($-a^*$) greenness, b^* represents the position ($+b^*$) yellowness/($-b^*$) blueness. Total colour difference (ΔE) values were calculated according to Equation (2):

$$\Delta E = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2} \quad (2)$$

where ΔL is the lightness difference between the samples, Δa is the redness difference between the samples, and Δb is the yellowness difference between the samples.[7,37]

2.2.7 | The pH response against bacterial solutions

The colour changes and pH responses were also tested against *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 6538). For both bacteria, solutions were separately prepared as 0.5 McFarland (10^8 CFU/ml) in Fluid Thioglycollate Medium (FTM) used as a general-purpose medium for bacteria according to ASTM E2149. They were dispensed as 2 ml into tubes, and the pH values of the tubes were checked at different times. After contact with solutions, the colour changes of the nanofibre mats were also visually inspected depending on bacterial growth because of the sample contamination.

2.2.8 | On-site application

This study aimed to produce a pH-sensitive sensor for instant measurement of pH, especially for food freshness detection. Therefore, the on-site performance of the electrospun sensor was evaluated on chicken breast. The anthocyanin-loaded sample with the best properties was used on-site application. For the experiment, a fresh chicken breast was purchased from a local market and kept at $20 \pm 2°C$ for 3 days. A piece of the selected anthocyanin-loaded nanofibre mat was placed on the chicken breast each day, and the colour change of the sample was photographed with a camera. A fresh pH sensor sample was used in each measurement.

3 | RESULTS AND DISCUSSION

3.1 | Solution characterisation

The viscosity of a solution is one of the most critical parameters affecting the electrospinning process and the properties of the nanofibre mats. It is known that low viscosity results in thinner but beaded nanofibres. Thicker and bead-free structures are obtained with increasing viscosity.[38]

The viscosity values of the solutions are given in Table 2. It can be seen that anthocyanin addition into the PCL/PEG solution caused a decrease in the viscosities. This may be due to the decreasing polymer concentration per unit volume after adding anthocyanin.[15] Another reason for the decrease in the viscosity may be the weakening of the bonds with the addition of anthocyanin.[39]

Although anthocyanin addition lowered the viscosity, the viscosity of the solutions was increased with the increasing anthocyanin in the solution, which might be due to the new strong interactions between the anthocyanin and the polymer solution[40] or the excessive amount of anthocyanin, which could not be dissolved in the polymer solution. The insolubility and precipitation of anthocyanin were visible to the naked eye during electrospinning, especially at higher concentrations, resulting in a more challenging fabrication.

Table 2 shows the pH values of the distilled water, anthocyanin-added distilled water, PCL/PEG, and anthocyanin-loaded PCL/PEG solutions. One can see that a significant pH decrease occurred both in distilled water and PCL/PEG solutions upon adding the anthocyanin. This points out that the acidic nature of anthocyanin leads to a decrease in the pH values. The acidity usually arises during the extraction processes of anthocyanins since acids such as hydrochloric acid are used. The anthocyanins might have residual acidity derived from the extraction process, which causes a decrease in the pH value of the polymer solutions.[41]

3.2 | Nanofibre characterisation

The SEM images of the nanofibre mats are given in Figure 2. PCL/PEG showed uniform nanofibres with an

Sample	Viscosity (cP)	pH	Average diameter (nm)
PCL/PEG	86.4	7.6	449 ± 204
PCL/PEG/1%ACN	60.8	5.0	288 ± 910
PCL/PEG/2%ACN	66.5	4.7	328 ± 244
PCL/PEG/3%ACN	75.7	4.4	354 ± 122
PCL/PEG/5%ACN	81.1	4.3	395 ± 144
Distilled water	—	7.1	—
Anthocyanin/distilled water	—	3.5	—

TABLE 2 Solution characterisation and average diameters of the nanofibre mats.

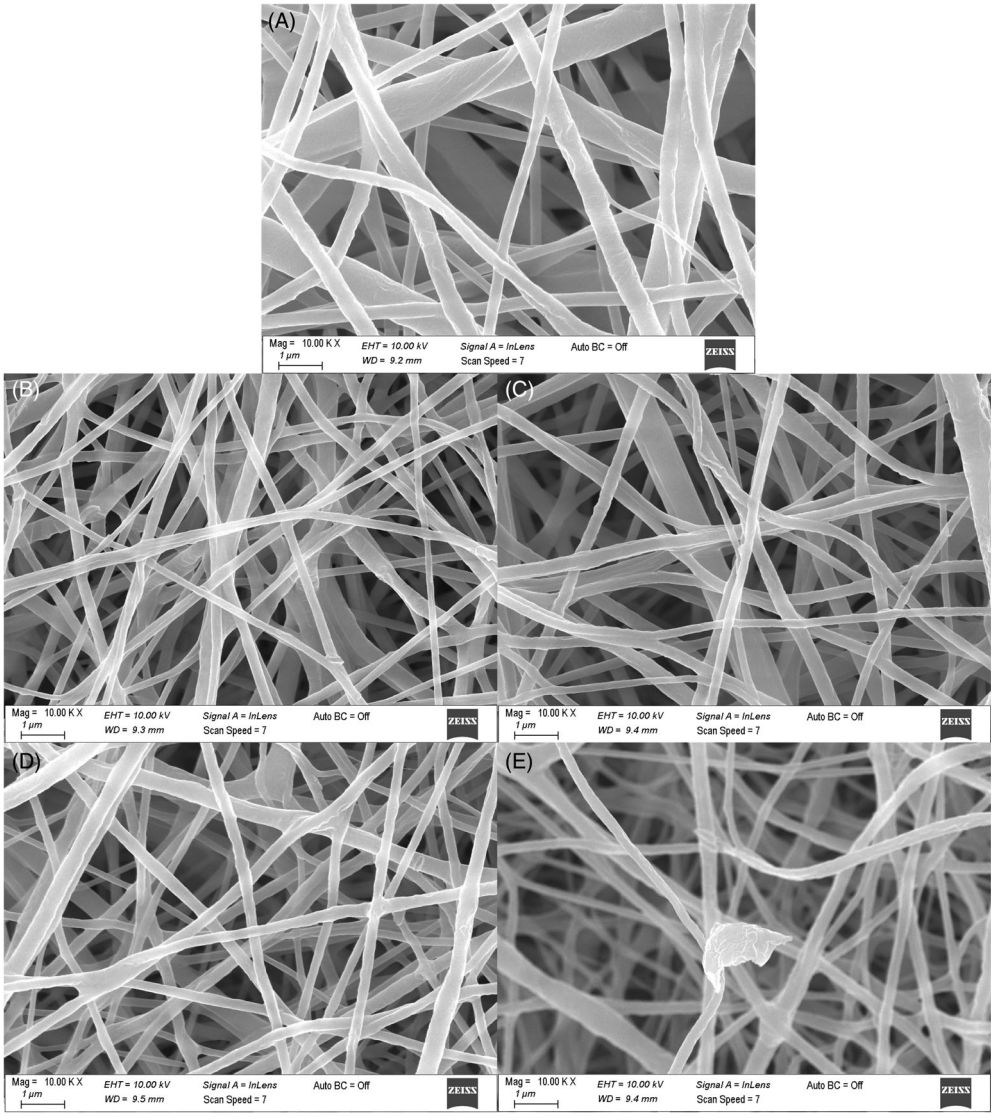


FIGURE 2 SEM images fibre diameter distribution of PCL/PEG (A), PCL/PEG/1% ACN (B), PCL/PEG/2%ACN (C), PCL/PEG/3%ACN (D), and PCL/PEG/%5ACN (E).

average diameter of 449 nm. As noticed in Table 2, mean nanofibre diameters decreased to 288 nm with the addition of anthocyanin. Moreover, the increase in the anthocyanin concentration caused an increase in the nanofibre diameters. PCL/PEG/5%ACN gave the highest nanofibre diameter of 395 nm among other samples. This can be explained by the viscosity changes caused by the addition of anthocyanin.

In addition, some agglomerates within the nanofibre mats were observed in all PCL/PEG/ACN samples, although it was more intensive in PCL/PEG/5%ACN. This might be either the jet instability caused by the high anthocyanin concentration during electrospinning or the insolubility of the anthocyanin in the spinning solution.[42] Also, electrospinning from this solution was challenging due to the solidification of the solvent at the tip and the

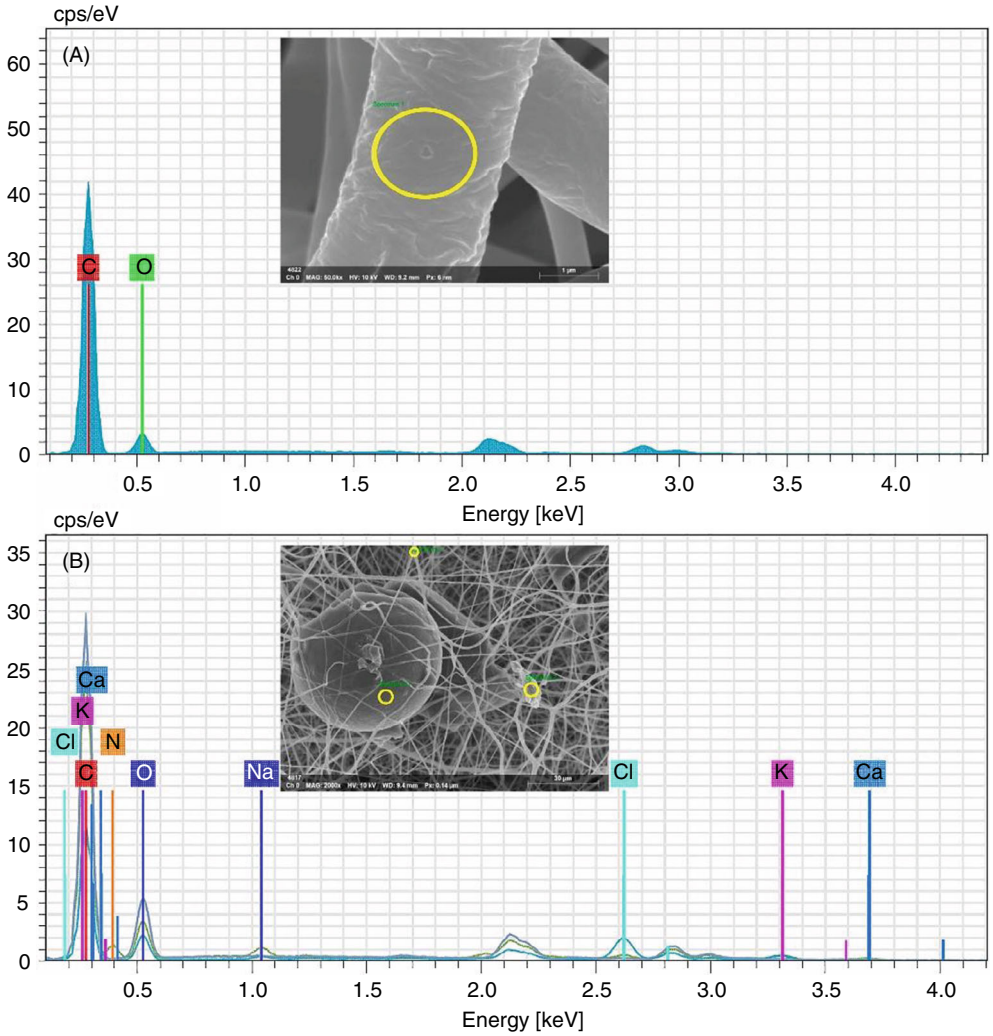


FIGURE 3 EDS spectra of PCL/PEG (A) and PCL/PEG/ACN (B).

precipitation of the anthocyanin in the syringe. This might cause an increasing number of agglomerates within the nanofibre mats. SEM analyses revealed that the highest anthocyanin concentration was 3% which can be added to the nanofibre structure without any precipitation during electrospinning. These samples showed nanofibre diameters around 350 nm with smooth nanofibre surfaces without beads or less excessive anthocyanin agglomerates within the nanofibre mats.

Elemental analyses were performed on the nanofibre mats and agglomerates, and the results are presented in Figure 3 and Table 3. Carbon and oxygen elements were detected on PCL/PEG nanofibre mats. The anthocyanin presence in the nanofibre structure was also confirmed by EDS analysis. Carbon, oxygen, and nitrogen were determined on PCL/PEG/ACN nanofibre mats. Carbon, oxygen, nitrogen, sodium, chlorine, potassium, and calcium were detected on PCL/PEG/ACN particles which are structural elements of anthocyanins.[14]

FTIR spectra of PCL, PEG, and PCL/PEG nanofibre mats are indicated in Figure 4 and Table 4, respectively. For PCL, the peaks at 2941, 2868, 1292, 1239, and 1161 cm^{-1} represent the characteristic peaks of the polymer.[43,44] The peaks at 3500, 2874, 1093, and 960 cm^{-1} point out the characteristic peaks of PEG.[45] In the PCL/PEG spectrum, the characteristic peaks of both PCL and PEG can be seen, indicating that PEG is successfully integrated with PCL.

The FTIR spectra of anthocyanin and PCL/PEG/ACN nanofibre mats are reported in Figure 5 and Table 5. In particular, anthocyanin has an absorption in the 3100-3400 cm^{-1} (OH stretching), 3000-2800 cm^{-1} (C–H stretching in the aromatic ring), 1800-1600 cm^{-1} (C=C stretching in the aromatic ring), 1200-900 cm^{-1} (C–O–C), and 675-870 cm^{-1} (C–H aromatic).[46,47] These band ranges are closely related to anthocyanin structures with aromatic rings, which bound oxygen-containing heterocyclic rings in addition to being bound by other aromatic rings through carbon-to-carbon bonds.[48] FTIR spectrum demonstrated that dyestuff has hydroxyl, alkane, and aromatic groups pointed to anthocyanin. The peaks at 3284, 2892, and 1016 cm^{-1} are the characteristic peaks of anthocyanin.

TABLE 3 Elemental analyses of the nanofibre mats.

Element	PCL/PEG nanofibre	PCL/PEG/5%ACN nanofibre	PCL/PEG/5%ACN agglomerate
Carbon	83.87	71.87	67.70
Oxygen	16.13	25.02	18.70
Nitrogen	—	3.11	4.39
Chlorine	—	—	5.37
Potassium	—	—	2.69
Sodium	—	—	0.58
Calcium	—	—	0.58

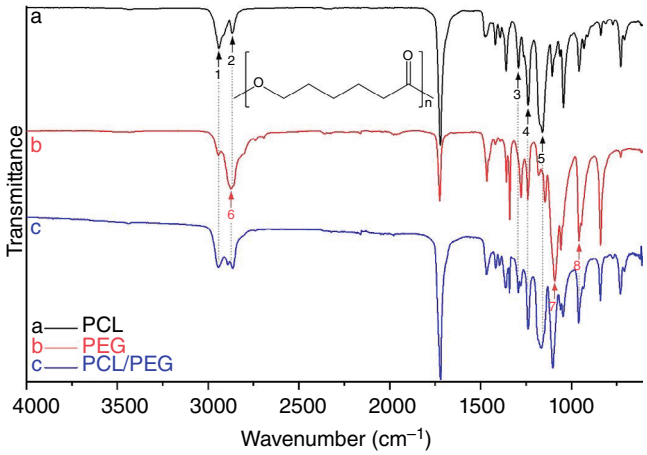


FIGURE 4 FTIR spectra of PCL (A), PEG (B), and PCL/PEG (C).

TABLE 4 FTIR spectra of PCL and PEG.

Peak number	Specific wavelength (cm^{-1})	Chemical bond
PCL		
1	2941	Asymmetric CH_2 stretching
2	2868	Symmetric CH_2 stretching
3	1292	C–O and C–C stretching
4	1239	Asymmetric COC stretching
5	1161	OC–O stretching
PEG		
6	2874	CH stretching
7	1093	C–O stretching
8	960	CH_2 stretching

The characteristic peaks for PCL, PEG, and anthocyanin were separately detected on nanofibre mats. These peaks show the presence of anthocyanin in the structure.

FTIR spectra can also reveal the chemical interactions between PCL and anthocyanin. One of the reactions that can occur between these two components is the transesterification reaction. As can be seen from the FTIR results, there are hydroxyl groups in the anthocyanin structure that can interact with PCL resulting in by-products such as ester and water.[49] In this study, these groups could not be identified by FTIR analyses.

Wettability is a significant property of a pH sensor, and it can easily be determined by contact angle measurements. The contact angle values above 90° indicate a hydrophobic character.[50]

The contact angle values are given in Figure 6. It can be clearly seen that PCL has a contact angle value of 119° which represents the hydrophobic character of PCL. In this study, the hydrophobic nature of PCL was modified by adding a water-soluble PEG polymer. Moreover, adding anthocyanin caused a decrease in the contact angle values, and this case pointed out that the nanofibre mats became more hydrophilic with the increasing anthocyanin concentration.

Apart from water-soluble components, contact angle values are also highly affected by the surface properties of the sample. The surface roughness, the nanofibre alignment, the porosity, and the pore size of the samples have critical effects on the contact angles.[51–53]

The fibre diameters and morphologies were also affected by the increasing anthocyanin concentration. These changes may have also contributed to the decrease in the contact angle values.

3.3 | Tensile tests

The mechanical properties of the nanofibre mats were determined by the tensile test, and the results are given in Table 6 and Figure 7. It can be noticed that anthocyanin addition enhanced the mechanical properties by increasing the modulus and stress while lowering the elongation for all samples. The highest modulus was obtained with the

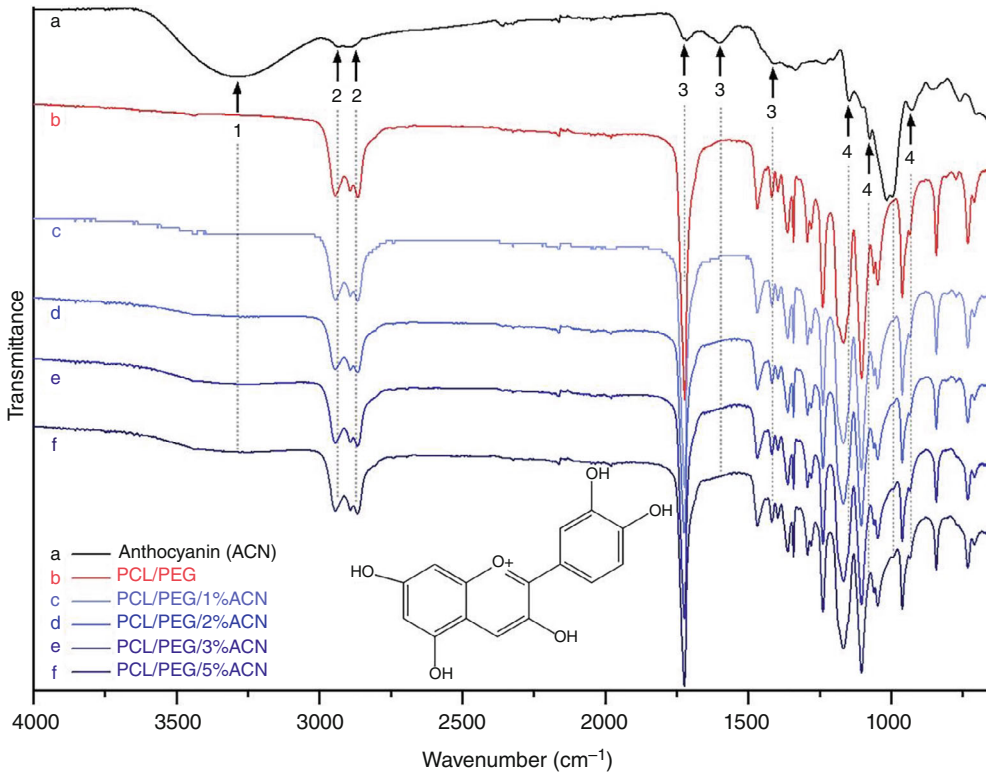


FIGURE 5 FTIR spectra of anthocyanin (ACN) (A), PCL/PEG (B), PCL/PEG/1%ACN (C), PCL/PEG/2%ACN (D), PCL/PEG/3%ACN (E), and PCL/PEG/5%ACN (F).

TABLE 5 FTIR spectrum of anthocyanin.

Peak number	Specific wavelength (cm^{-1})	Functional group—chemical bond
Anthocyanin		
1	3284	O–H stretching
2	2934, 2892	CH stretching in the aliphatic structure
3	1716, 1602, 1405	C=C– stretching in the aromatic ring structure
4	1147, 1076, 1016, 927	C–O–C stretching

sample loaded with 1% anthocyanin. The anthocyanin might act as the plasticiser and reduce the macromolecule interactions, resulting in a higher modulus.[54] The mechanical properties tend to decrease with the increasing anthocyanin concentration. However, the modulus values were still higher than the samples without anthocyanin, proving that mechanical properties were improved.

3.4 | Release experiments

Release experiments were performed to understand the release behaviour of anthocyanin from the nanofibre

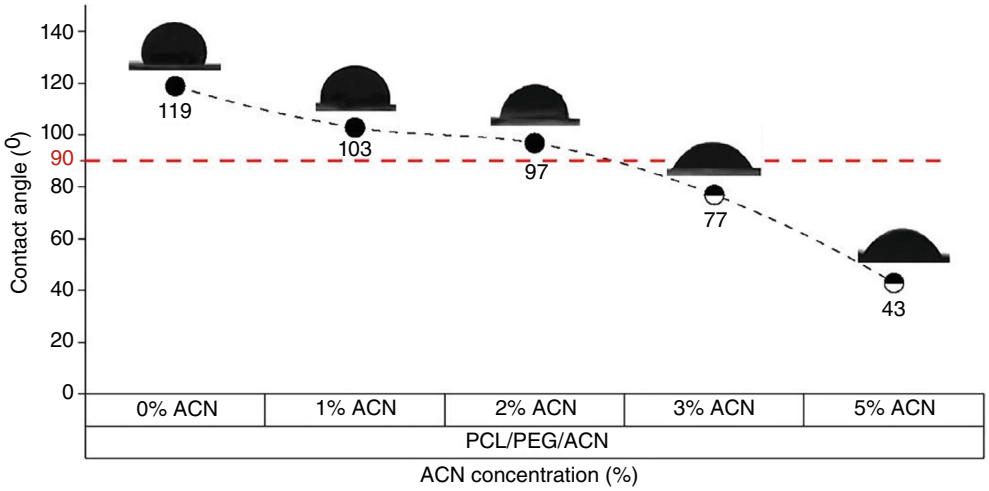


FIGURE 6 Contact angles of PCL/PEG and PCL/PEG/ACN nanofibre mats.

TABLE 6 Mechanical properties of the nanofibre mats.

Samples	Thickness (mm)	Stress (MPa)	Elongation (%)	Modulus
PCL/PEG	0.123 ± 0.070	1.016 ± 0.269	67.138 ± 5.223	2.735 ± 1.048
PCL/PEG/1%ACN	0.110 ± 0.012	2.425 ± 0.158	63.752 ± 10.266	6.162 ± 0.436
PCL/PEG/2%ACN	0.108 ± 0.027	2.024 ± 0.408	57.445 ± 8.099	4.980 ± 1.147
PCL/PEG/3%ACN	0.074 ± 0.004	1.957 ± 0.249	57.158 ± 8.301	4.885 ± 1.027
PCL/PEG/5%ACN	0.098 ± 0.010	1.350 ± 0.315	45.468 ± 7.756	3.590 ± 0.734

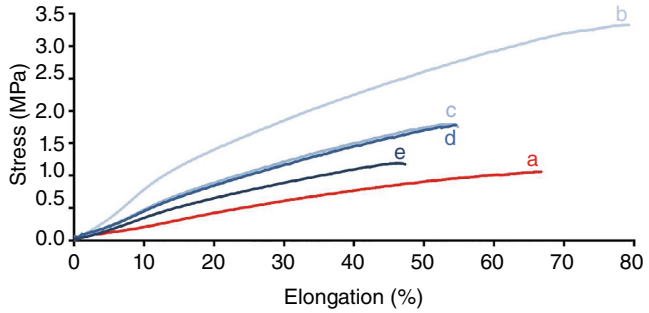


FIGURE 7 The stress-elongation curves of the samples: PCL/PEG (A), PCL/PEG/1%ACN (B), PCL/PEG/2%ACN (C), PCL/PEG/3%ACN (D), and PCL/PEG/5%ACN (E).

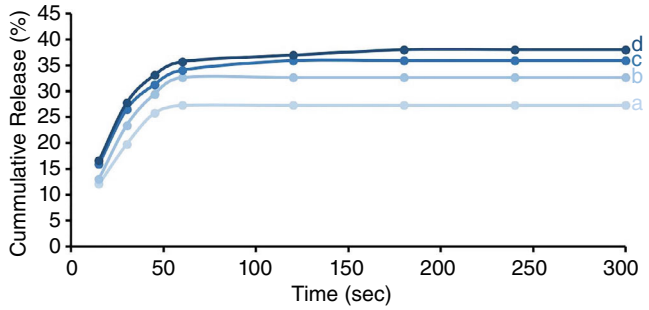


FIGURE 8 Anthocyanin release from the samples: PCL/PEG/1%ACN (A), PCL/PEG/2%ACN (B), PCL/PEG/3%ACN (C), and PCL/PEG/5%ACN (D).

mats. Figure 8 shows the results of the release studies. It can be observed that 12.07%, 13.07%, 15.92%, and 16.62% of anthocyanin were released from the samples loaded with 1%, 2%, 3%, and 5% anthocyanin in the first 15 s, respectively. All samples showed a fast release rate indicating that the response time of these samples would be also fast when they interact with a liquid. According to Figure 8, a burst release occurred in the first minute, and a more gradual release was seen afterward. The burst release may be related to the anthocyanin present on the surface of the nanofibres and the porous structure of the nanofibre mats.[55] At the end of the 300 s, 38.02%, 35.86%, 32.66%, and 27.30% of anthocyanin were released from the samples loaded with 5%, 3%, 2%, and 1% anthocyanin,

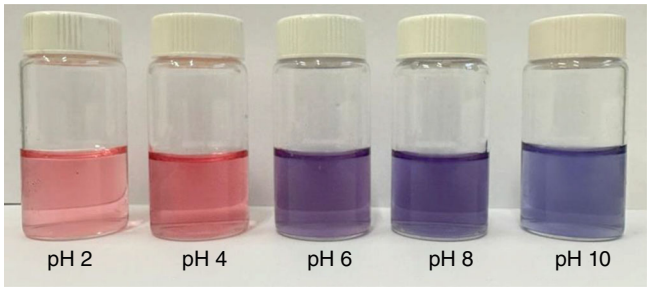


FIGURE 9 Colour changes of the (0.04%) anthocyanin-added solutions with different pH values.

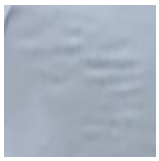
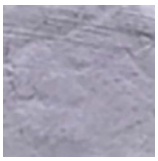
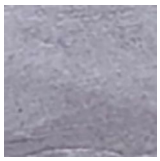
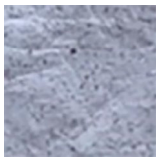
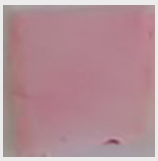
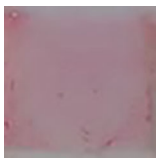
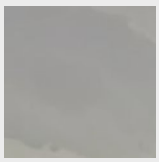
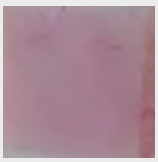
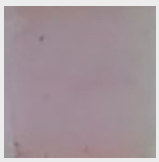
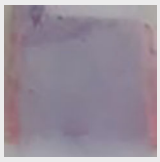
respectively. The higher release rate of PCL/PEG/5%ACN could be due to the higher and excessive anthocyanin content within the nanofibre mat. The videos of the samples exposed to different pH solutions are given as Supporting Information Videos S1-S4 to show the response of the anthocyanin-loaded samples.

3.5 | The pH response and colorimetric analyses

Anthocyanins have well-known chemical structures that change colour highly sensitively to solutions with different pH values. In general, pink-red colour is observed at low pH values (pH 2), while it turns into blue-violet and yellow at high pH values (pH 3-10).[54] Figure 9 shows the colour change of the anthocyanin-added solutions with different pH values. The colour change from pink to purple can be clearly seen.

The colour changes of the nanofibre mats depending on different pH values are demonstrated in Table 7. Initially, considerable colour difference was not visually observed in PCL/PEG nanofibre mats after contacting them with different pH solutions. However, visually distinguished colour changes were observed on anthocyanin-loaded PCL/PEG nanofibre mats when compared with PCL/PEG. The white colour of the reference turned to light red-pinkish with the increasing anthocyanin concentration. At the same time, colour changes were clearly visible in PCL/PEG/ACN nanofibre mats. As seen in Table 7, red

TABLE 7 Colour changes of the nanofibre mats depending on different pH values.

	Samples				
		PCL/PEG/ACN			
pH	PCL/PEG	1%ACN	2%ACN	3%ACN	5%ACN
Reference					
2					
4					
6					
8					
10					

and blue colours were seen at low pH values (pH 2) and high pH values (pH 10), respectively. In here, transition tones between these two colours were noticed at intermediate pH values. Consequently, the visual analyses clearly showed that PCL/PEG nanofibre mats with 2% and 3% anthocyanin were the most capable pH-sensitive sensor for detecting pH changes from pH 2 to 8.

The colour values measured spectroscopically are displayed in Figure 10. Firstly, the remarkable difference in all colour values (L^*, a^*, b^*, and ΔE) was not spectroscopically observed in PCL/PEG nanofibre mats after contacting them with different pH solutions. However, L^* values naturally and proportionally decreased from 94.2 to 81.4, and darker colours were obtained with the increasing anthocyanin concentration considering PCL/PEG as reference. In addition, after contact with solutions, the changing pH values caused a further decrease in L^* values.

Compared with the reference, a^* values increased from −0.3 to 2.8 after adding anthocyanin into PCL/PEG nanofibre mats. These values showed an increasing trend with the increasing anthocyanin concentration. The positive ($+a$) values are meant that the colour shifted towards the red side in colour space. After that, the changing pH values brought about a noticeable and characteristic difference in a^* values.

The b^* values decreased from 1.2 to −0.4 after adding anthocyanin. These values displayed a decreasing trend with the increasing anthocyanin concentration because of the nature of the dyestuff. The negative ($-b$) values are meant that the colour shifted towards the blue side in

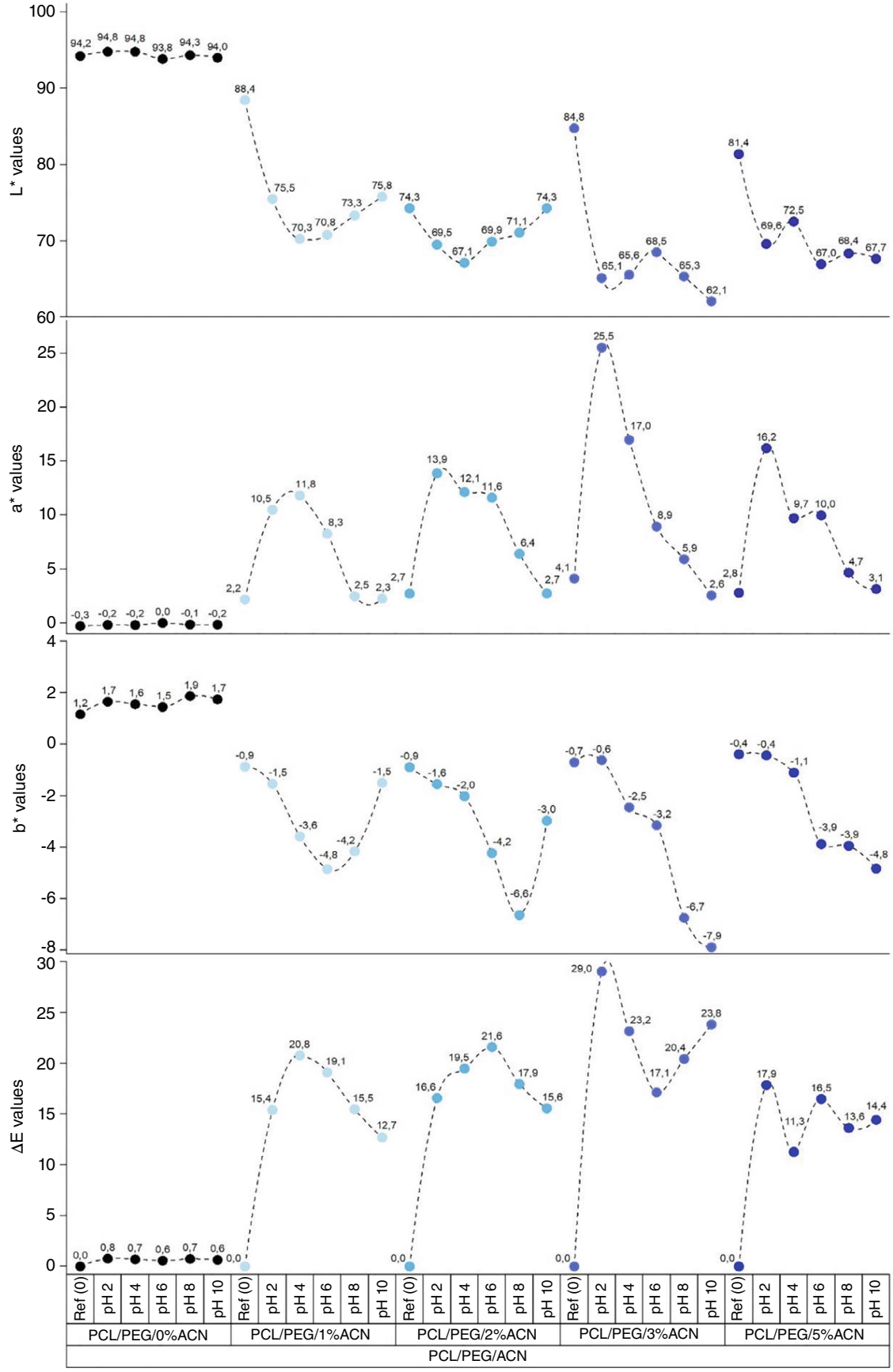


FIGURE 10 Colour values of the nanofibre mats depending on different pH values.

colour space. At the same time, the changing pH values caused distinguished changing in the b^* values.

Among the parameters of colour differentiation, the total colour difference (ΔE) is considered one of the most important.[30] The notable ΔE values were spectroscopically detected in all PCL/PEG/ACN nanofibre mats after contacting them with different pH solutions, and they had values greater than 5. This indicates that colour differences can be seen easily by the naked eye. Surprisingly, the PCL/PEG/ACN nanofibre mats responded better to pH changes at lower concentrations (1%, 2%, and 3%) but differentiated at higher concentrations (5%).

Consequently, it is found that the colour values measured spectroscopically were compatible with the colour changes observed visually. And it was figured out that PCL/PEG nanofibre mats with 2% and 3% anthocyanin have promising pH-sensitive properties for detecting pH changes from pH 2 to 8.

3.6 | The pH response against bacterial solutions

Colour changes and pH responses of the nanofibre mats were tested against gram-negative (*E. coli*) and gram-positive bacteria (*S. aureus*). For pH response against bacterial solutions, in the beginning, both bacteria concentrations were separately prepared as 0.5 McFarland (10^8 CFU/ml). Therefore, bacterial concentration did not increase depending on time. The pH changes have been measured in broth over time depending on time (bacterial growths, deaths, and the metabolic wastes created by bacteria; pH changes are caused by them, not bacteria concentrations). For both bacteria, the pH values of the prepared bacterial solutions were checked at different times, and pH changes depending on bacterial growth are given in Figure 11. It is well known that heat easily affects anthocyanins and can degrade immediately after. To avoid this, both types of bacteria only stayed at 37°C in the shaking incubator for bacterial growth. At the same time, surfaces were just held in the laboratory at room temperature (20 ± 2°C) until the tests were performed. Since pH response studies were made at the room temperature, the samples were not exposed to higher temperatures (more than 27°C). Here, pH changes of FTM were used as the negative control. For both bacteria, it was evidently observed that there were sharp decreases in their pH from 7.30 to 5.00 and 5.13, respectively, after 15 h. The decrease in pH level over time is a normal phenomenon.[56]

After contact with bacterial solutions, the colour changes of the nanofibre mats were also visually inspected depending on bacterial growth because of the sample contamination. Sample images are demonstrated in Table 8. Initially, colour difference was not visually observed in PCL/PEG nanofibre mats after contacting them with the bacterial solution at pH 4.90 for *S. aureus* and 5.08 for *E. coli*, respectively. However, the colour changes were

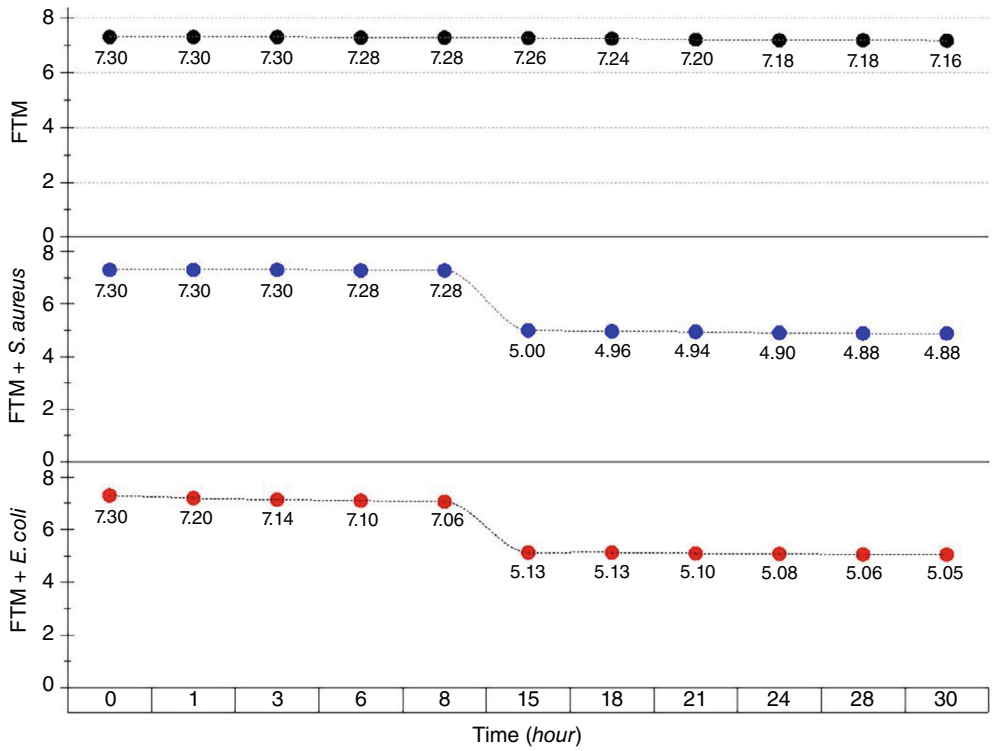
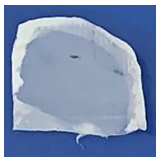
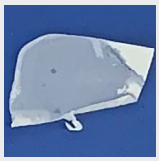
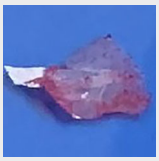


FIGURE 11 The pH changes depending on time.

TABLE 8 Colour changes of the nanofibre mats depending on bacterial growth.

	Samples				
		PCL/PEG/ACN			
pH	PCL/PEG	1%ACN	2%ACN	3%ACN	5%ACN
4.90 for *Staphylococcus aureus*					
5.08 for *Escherichia coli*					

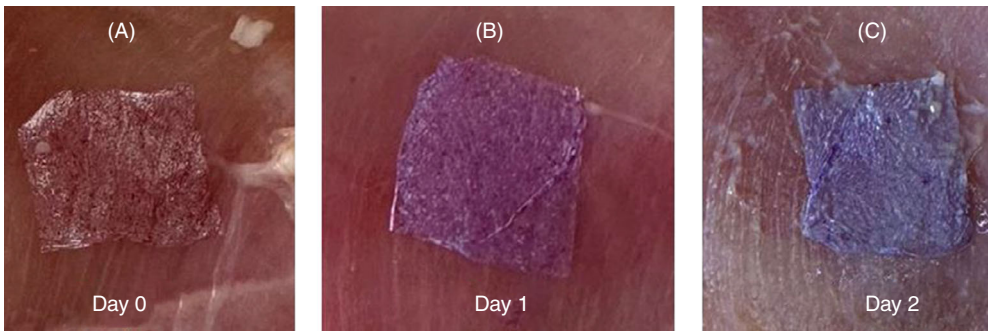


FIGURE 12 On-site application of the sensor: Day 0 (A), Day 1 (B), and Day 2 (C).

visually noticed depending on the adding anthocyanin into PCL/PEG nanofibre mats when compared with PCL/PEG as reference. The white colour of the reference turned to light red-pinkish with the increasing concentration. These results are compatible with visual analyses in Table 7. Consequently, the visual analyses obviously proved that PCL/PEG nanofibre mats with 2% and 3% anthocyanin were the most skilled sensor for detecting bacterial growth after 24 h.

3.7 | On-site application

In Figure 12, the on-site application of the pH sensor is shown. When the pH sensor was applied to the chicken breast, defined as Day 0, the sensor turned to a reddish colour, representing that the chicken breast was fresh. After 24 h (Day 1), the sensor became more pinkish, indicating that the pH was increased. After 48 h (Day 2), the sensor turned purple, remarking that the pH was very high and the chicken breast had deteriorated. The results evidenced that the anthocyanin-loaded nanofibres offer fast and accurate information and serve as pH sensors.

4 | CONCLUSIONS

This study aims to fabricate a pH-sensitive nanofibre mat for instant detection of pH, especially for determining food freshness. Therefore, PCL/PEG and PCL/PEG/ACN nanofibre mats were produced with different anthocyanin concentrations (1%, 2%, 3% and 5%) and characterised in terms of solution, surface, thermal, mechanical and release properties. The colour changes against pH changes and different bacterial solutions were evaluated. Finally, the on-site application of the selected sample was carried out to understand the performance of the anthocyanin-loaded nanofibre mat. Viscosity measurements showed that adding anthocyanin into the polymer solution caused a decrease in viscosity values. Furthermore, the viscosities were increased with the increasing anthocyanin concentration in the polymer solution. SEM images revealed that anthocyanin-loaded nanofibres were successfully electrospun and the increase in the anthocyanin concentration caused smaller nanofibres in diameter. Some agglomerates within the anthocyanin-loaded nanofibre mats were observed due to the excessive anthocyanin content. This was more intensive in the samples loaded with 5% anthocyanin. EDS and FTIR results confirmed the presence of

anthocyanin in the nanofibre structure. The samples with higher anthocyanin concentrations gave lower contact angles pointing out a more wettable surface. Anthocyanin addition also enhanced the mechanical properties and samples with higher modulus values were obtained compared to the sample without anthocyanin. The release experiments revealed that all the samples released a large amount of anthocyanin (between ~12% and 38%) in the first 15 s. Also, a burst release was seen for all samples in the first 60 s which can be proof of anthocyanin–liquid medium interaction. Apart from these, the colour changes were monitored by both spectrophotometer and the naked eye. Colour shift from red to blue was noted upon exposure from pH 2 to 10. The results showed that the maximum working concentration for this study was 3%. Surprisingly the sensor responded better to pH changes at lower concentrations (1% and 2%). The colour changes and pH responses of anthocyanin-loaded nanofibre mats against bacterial solutions showed that PCL/PEG nanofibre mats with 2% and 3% anthocyanin were the most skilled sensor for detecting bacterial growth after 24 h.

The overall results indicated that even smaller nanofibres with higher mechanical properties were obtained for the samples with lower anthocyanin concentrations. These samples have lower anthocyanin release properties, and the colour change against the pH changes was not clear to the naked eye. Therefore, the sample loaded with 3% anthocyanin was chosen for the on-site application due to its optimum properties with high anthocyanin content. The experiments were performed on a fresh chicken breast. It was seen that the colour of the sample turned from pink to purple, which showed that the chicken breast had deteriorated.

Instant pH detectors can be used, especially in monitoring the quality control process. The detector can show a rapid and noticeable colour change for instant tests to determine whether the cold chain of products that are stored for a long time or during food transportation is broken. As a result, it can be concluded that anthocyanin-loaded nanofibres can be used as pH sensors for fast and accurate information.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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