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Nanocellulose incorporated Polylactic Acid Films for chilled preservation of Indian Anchovy (*Stolephorus indicus*) (van Hasselt, 1823)

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Abstract

Polylactic acid (PLA) nanocellulose (NC) films were fabricated by compounding different levels (1%, 2% and 3%) of nanocellulose into the PLA matrix to improve the mechanical properties. The mixed PLA and NC of different percentage were extruded into tubular blown films using a co-rotating extruder. The films were analysed for different mechanical and physical properties. The addition of nanocellulose significantly improved the tensile strength and the heat sealing properties of the films. The water vapour transmission rate did not show much difference between the different levels of NC filler. The surface morphology of the obtained films was characterised by scanning electron microscopy (SEM). The compositional analysis was done by Fourier transform infrared spectroscopy (FTIR) and it revealed that nanocellulose interacted with PLA. *Stolephorus indicus (*anchovy) (van Hasselt, 1823) were packed in different PLA/NC films and kept in chilled condition for 20 days to evaluate the preservative effect. Biochemical parameters such as peroxide value, free fatty acid, trimethylamine, total volatile base nitrogen and microbial parameter such as total plate count were carried out during the storage period. The results proved that the fish samples packed in different PLA/nanocellulose films had better shelf life compared to neat PLA and LDPE films during the chilled storage.

Keywords: Polylactic acid, nanocellulose, films, Indian Anchovy, chilled storage

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Introduction

Packaging helps in retarding deterioration, extending shelf-life and maintaining inherent quality and characteristics while ensuring safety of the packaged food. Packaging protects from environmental factors like heat, light, moisture, oxygen, pressure, enzymes, microorganisms, insects, dirt and dust particles that causes deterioration of foods and beverages (Marsh & Bugusu, 2007). Polymer based packaging materials are produced from fossil fuels that are practically non-degradable. As an alternative biobased packaging material of plant origin is being explored to extend the shelf life and enhance food quality while reducing packaging waste. Biobased packaging materials, like edible and biodegradable films from renewable resource could solve the waste problem (Sorrentino et al., 2007). Development of biopolymers based packaging has been gaining more attention in recent decades due to environmental pollution, petroleum product price increase and concerns about global warming which has aroused much interest for alternatives (Barnes et al., 2009).

Biodegradable and renewable polymers have been increasingly studied for applications that are beneficial to the customers and environment (Chen & Patel, 2012). Polylactic acid (PLA) and polybutylene succinate (PBS) are the most promising thermoplastic polymers in this regard as they are compostable and suitable for consumer goods and packaging applications. Currently, biobased plastics are being used for biomedical devices, food packaging, agriculture and hygiene products. PLA has gained much interest in recent years because it is being commercially produced in large scale at a reasonable price and it has some unique properties such as high modulus and good heat seal ability. PLA

has also found applications in fast food service ware, grocery and composting bags, mulch films, and controlled release matrices for fertilizers, pesticides and herbicides (Tongnian et al., 2006). The major limitations of this biodegradable polymer is its poor thermal and mechanical resistance and limited gas barrier properties compared to petroleum based polymers, which limit its applications in packaging. The above drawbacks could be overcome by enhancing their thermo-mechanical properties through copolymerization, blending and filling techniques. For these reasons natural polymers are either blended with other synthetic polymers or reinforcing with natural fibres to their properties.

Nanocellulose (NC) has been proven to be one of the most promising green materials of recent times and has gained growing attention due to its attractive and excellent characteristics such as high aspect ratio, better mechanical properties, renewability, and biocompatibility (Trache et al., 2020). NC is used as a filler because of its mechanical properties (Fernandes et al., 2010) of providing reinforcement in composites, as well as its ability to produce flexible films. Nanocellulose is reported to have low toxicity and low environmental risk potential (Kovacs et al., 2010). The use of cellulosic particles as a reinforcing material in nanocomposites is advantageous due to its low density, renewable nature, availability of wide variety of fillers, low energy consumption, high specific properties, easy processing, biodegradability, relatively reactive surface, which can be used for grafting specific groups and almost unlimited availability (Azizi et al., 2004). Several authors have reported improvement in thermal and mechanical properties after the addition of natural fibers such as nanofibrillated cellulose (NFC) and cellulose nanocrystals (CNC), into polymer matrix (Souza et al., 2010; Pinheiro et al., 2019). These impressive properties make cellulose nanoparticles ideal candidates for reinforcement of polymer composites. The aim of the study was to fabricate and evaluate the mechanical and physical properties of a biobased film from PLA with nanocellulose (PLA/NC) in different composition and for exploring the possibility of using PLA nanocellulose film as a material for packing Indian Anchovy, (*Stolephorus indicus*). The study also looked into determining their shelf life in the chilled condition in comparison with neat PLA and LDPE film.

Materials and Methods

Polylactic acid (PLA) resin grade (Ingeo-4043 D) supplied by Nature works LLC was used in this study. The density of the polymer was 1.24 g cc^{-1} (ASTM D-1505), with the melt flow of 3.498 g 10 min^{-1} (ASTM D-1238) and melting temperature (Tm) of 145-160°C. Nanocellulose (NC) fibres were obtained from ICAR-CIRCOT, Mumbai and used as fillers for the films. The blend preparation and film production was done as per the method described by Reesha et al. (2015) and Fathima et al. (2018). Initially predrying of the PLA and NC was done at 80°C for six hour before mixing and compounding. Composite blend formulations were prepared by mixing PLA as matrix material and NC as filler material at 1, 2 and 3% level. The compounding of PLA/NC was carried out in a co-rotating twin screw extruder with a screw diameter of 21 mm and L/D ratio of 40:1 at maximum speed of 72 rpm at melt temperature of 191°C. The extruded pellets were smooth and bubble-free and exhibited different colours due to the concentration of the nanocellulose (Fig. 1). The compounded materials and neat PLA were melted at a melt pressure of 96 and melt temperature of 146°C and blown into a tubular film in a monolayer extruder (Konark Plastomech Pvt. Ltd) The screw speed of the extruder was 320 rpm and the barrel temperature was 186°C.

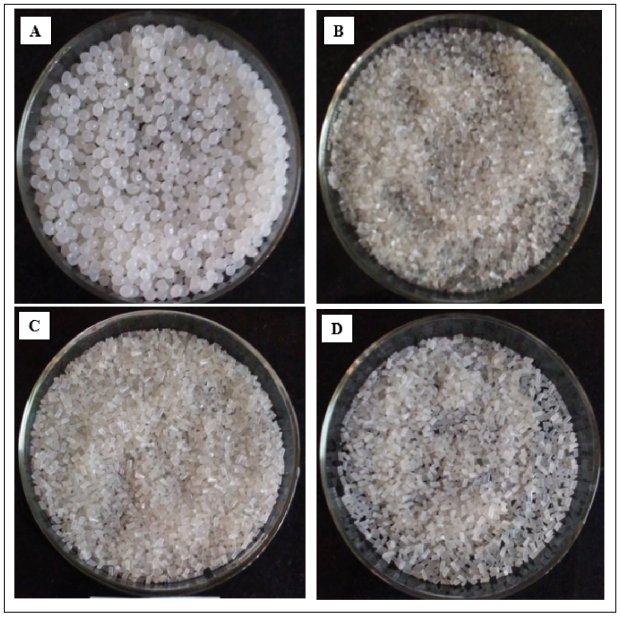

Fig. 1. Nanocellulose reinforced PLA (A) Neat PLA (B) PLA with 1%, (C) 2% and (D) 3% Nanocellulose

Thickness of the films were measured as per IS:2508 using gauge meter (Mitutoyo, model No: 2046-08). The percentage of transparency of the films was calculated by haze meter (ASTM D-1003). Surface morphology were examined by using Scanning Electron Microscopy (JEOL Model JSM - 6390LV) at STIC (Sophisticated Test and Instrumentation Centre, CUSAT, Kochi). The tensile strength, heat seal strength and elongation at break of different PLA/NC films were evaluated using Lloyd instruments UK, model TA plus according to ASTM D882-02(2002). The water vapour transmission rate was measured by Lyssy water vapour permeability tester (PBI Dan sensor Denmark, Model L80-5000). ASTM E398 (2003). The DSC experiments were performed in a TA Q20 DSC apparatus, using a refrigerator-cooling accessory and nitrogen as a purge gas. Fourier transform infrared (FT-IR) spectra of different concentrated PLA/NC films were carried out in Thermo Nicolet, Avatar 370 FTIR spectrometer, at STIC (Sophisticated Test and Instrumentation Centre, CUSAT, Kochi). Scanning was performed at 4 cm^{-1} resolutions. The measurements were recorded between 4000 and 400 cm^{-1}.

Indian anchovy (*Stolephorus indicus*) belonging to the Class – Actinopterygii, Order - Clupeiformes, and Family - Engraulidae were used for the study. The fish was purchased from the landing centre at Kalamukku, Kochi and iced and transported to the laboratory in chilled condition in insulated boxes. Fish was then beheaded, gutted, cleaned and washed in potable water. About 100 g of dressed fish each was packed in the different PLA / NC films and kept in insulated container with ice for storage at 2 ±1°C. Fish was also packed in LDPE and plain PLA film which were kept as control. The shelf life of fishes packed in different concentration of PLA/NC films under chilled storage was evaluated over the period of time.

The pH was determined using a pH meter (Merck) as described by APHA (1998). Total volatile base nitrogen (TVBN) and trimethylamine (TMA) was determined by micro diffusion method (Conway, 1962). Free fatty acid was analysed as per the AOAC method (2002), Thiobarbituric acid value (TBA) was measured as per the method prescribed by Tarladgis et al. (1960). The aerobic plate count (APC) was estimated by using a dry rehydratable film (Petri film aerobic plate count), method as per AOAC (2012). Sampling was done in triplicate and the values were expressed in Mean ± Standard Deviation (SD) for analysis.

Results and Discussion

The blown films (PLA/NC) and neat PLA films varied with thickness and morphology. The thickness (mm) of different PLA/NC films is shown in Table 1. Films exhibited good process- ability at a temperature of 186°C. There was no significant difference between the neat PLA and different concentration of PLA/NC film with regard to the thickness. The thickness was deeply influenced by the filler, the processing conditions and mixing of the filler into the matrix.

Table 1. Physical properties of PLA & NC films

Properties of films	Neat PLA	PLA / 1% NC	PLA / 2% NC	PLA / 3% NC
Film Thickness (mm)	0.065±0.001	0.069±0.006	0.064±0.00	0.066±0.00
Transparency (%)	91.26±0.01	89.08±0.01	89.04±0.01	88.40±0.005
Tensile strength (kg cm^{-2}) (Machine Direction)	408.23±0.01	411.87±0.01	469.18±0.01	512.82±0.005
Elongation at break (%) (Machine direction)	2.63±0.01	2.74±0.005	2.95±0.01	3.06±0.005
Heat seal Strength (kg cm^{-2})	80.95±0.01	80.97±0.005	86.35±0.005	87.17±0.01
Water vapour transmission rate (g m^{-2}*day)	3.77±0.01	3.65±0.005	3.51±0.01	2.64±0.01
Overall migration residue (mg l^{-1})	2.01±0.02	12.10±0.01	12.40±0.005	13.70±0.005

* Results are expressed in Mean±SD (n=3)

The transparency of different concentration of PLA/NC films are shown in the Table 1. Neat PLA had the transparency percentage of 91.26±0.01. Whereas in PLA/NC films the percentage of transparency decreased gradually (89.08±0.01 to 88.40±0.005) with increasing concentration of nanocellulose. This may be due to the fact that, high amount of nanocellulose disturbed the packing blend system, making it more disordered and uneven with higher free volume, thus more light can diffuse back or reflected.

The SEM images of neat PLA and PLA/NC films are given in the Fig. 2. PLA showed a smooth and uniform surface typical of a semi crystalline polymer, as observed by Yang et al. (2015). In PLA/NC films, the surfaces of specimens with different concentrations of NC showed a different microstructure. At lower concentration (1%) the films showed relatively small aggregations of nanocellulose with less roughness, whereas as the nanocellulose concentration increases, its showed that some of the aggregates were evident and a relatively rougher surface.

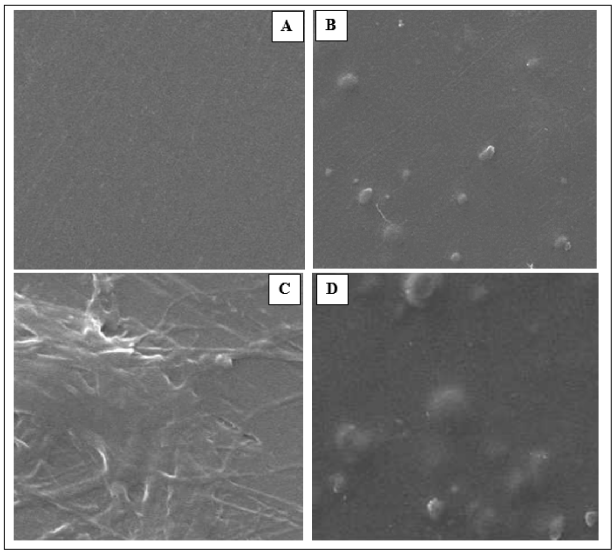

Fig. 2. SEM image at resolution of 20 kv 1500X (A) Virgin PLA (B) PLA / 1% NC (C) PLA / 2% NC (D) PLA / 3% NC

DSC was used to investigate the glass transition, crystallization and melting phenomena of neat PLA and PLA/NC bio nanocomposites (Fig. 3). There is no significant variation in the glass transition temperature (Tg) and melting temperature (Tm) by addition of NC into PLA compared to neat PLA. Neat PLA shows Tg about 63.86°C and Tm 152.04°C but with addition of nanocellulose it decreased to 63.34°C and the melting point slightly increased to 154.37°C. Moreover, there were two melt peaks in the DSC curve, suggesting that addition of NC promoted the rearrangement of PLA segments and the formation of heterogeneous crystal phases in PLA during thermal crystallization (Shih et al., 2010). Double melting peaks or endotherms were observed at low temperature of about 148.46°C and higher melting peaks at 154.37°C. Nanocellulose acts as a nucleating agent and promotes the formation of small and imperfect crystals that change into more stable crystals through melting and recrystallization at low heating rates or to lamellar populations with two different crystalline phases (Bitinis et al., 2013).

FTIR spectroscopy was employed to investigate the interfacial interaction between PLA and different concentrations of NC. As shown in the Fig. 4, the IR spectrum of NC showed three characteristic peaks at 2873 cm^{-1}, 1452 cm^{-1} and 1375 cm^{-1} corresponding to the C-H stretching, -CH_2 bending, C-H bending respectively. The peak at 1086 cm^{-1} is related to C-O stretching. In addition, the peak at 1641 cm^{-1} belongs to –OH bending of absorbed water, because the water absorbed by cellulose molecule is too difficult to extract. (Abdelmouleh et al., 2007; Shih et al., 2010; Valadez et al., 1999). The stretching and bending peaks of CP%O appear at 1726 cm^{-1} and 1222 cm^{1} respectively. With the addition of nanocellulose the CP%O peak of PLA at 1729 cm^{-1} become wider than that of pure PLA which indicate that hydrogen bond has formed between CP%O of PLA and –OH group of nanocellulose.

The variation of tensile strength and elongation at break of PLA/NC films and neat PLA films are given in Table 1. Tensile strength and elongation at break of PLA/NC blends increased with increasing concentration of nanocellulose. The increase in the tensile strength of PLA/NC films is mainly attributed to the addition of NC into PLA, which caused increased PLAs crystallinity and reduced the loading force on PLA through the stress transfer from PLA to CNCs (Zhou et al., 2011). This result also describes uniform distribution of the filler into the matrix. (Casper et al., 2004; Xiang et al., 2009). The elongation at break of PLA/NC films increased on addition of nanocellulose which may be attributed to the increased dispersion and interfacial adhesion of nanocellulose to PLA matrix (Lönnberg et al., 2011; Lin et al., 2009). Heat sealing strength (Table

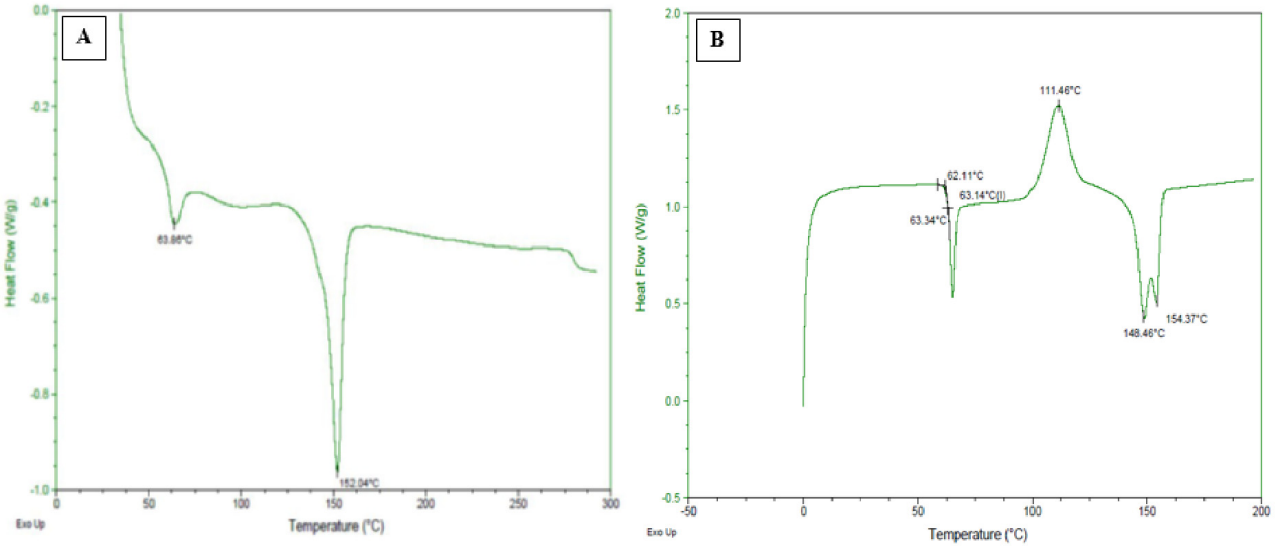

Fig. 3. (A): DSC curve of Neat PLA, (B): DSC curve of PLA/NC film

1) is an important property for food packaging application which determines the package integrity of the product. The heat seal strength of PLA films and PLA/NC films exhibited good heat sealability which increased slightly with addition of nanocellulose.

The water vapour transmission rate of the films are given in Table 1. In this study PLA/NC films were having lower WVTR than neat PLA films. It is well known that the transport properties of gases through polymer films are strongly influenced by the tortuosity of their path, which is dependent on several factors including shape and aspect ratio of the filler, degree of dispersion, filler loading and its orientation, adhesion to the matrix, moisture activity, crystallinity, polymer chain immobilization, filler-induced solvent retention and porosity (Sanchez-Garcia et al., 2008). In our case, the nanocellulose based nanocomposites were dispersed to a higher extent as showed in SEM analysis and possessed higher levels of crystallinity, thus yielding a more efficient barrier effect.

The overall migration of nanocellulose incorporated PLA films satisfied the limit value of OMR (Table 1). NC/PLA films with 3% shows a higher value of OMR (13.70±0.005 mg l^{-1}). The overall migration of these films were within the OMR limit of 60 mg l^{-1}. So these films were found suitable for food contact application.

The pH of initial sample was recorded at 6.22 and values increased slightly to 6.66, 6.63, 6.62, 6.64, and 6.65 for the samples packed in PLA, LDPE, and PLA/NC 1%, 2%, and 3% respectively at end of storage (Fig. 5A).

The initial TVB-N values of samples packed in PLA/NC 1%, 2%, 3%, Neat PLA & LDPE were 6.30± 0.99 mg 100 g, which gradually increased with increase in storage days (Fig. 5B) and finally reached the value of 19.07±0.90, 18.41±00, 18.09±1.98, 18.14±0.99, 17.84±1.98 mg 100 g^{-1} samples respectively at the end of 20 days of storage. In the present study, TVB-N values for all the samples were within the acceptability limits of 35-40 mg% (Connell, 1980). TVB-N products of bacterial spoilage and their contents are often used as an index to assess the keeping quality and shelf life of fish products (Lannelongue et al., 1982).

TMA is an excellent indicator for the onset of spoilage and for determining the different stages of spoilage of seafood. TMA was not detected in the initial days but started increasing from 5th day of storage onwards and finally reached to 4.90±00, 3.50±0.99, 4.90±00, 4.900±00, 3.50±00 mg 100 g^{-1} of TMA for PLA/NC 1%, 2% 3% Neat PLA & LDPE respectively (Fig. 5C). The results indicated that, TMA was produced at very low concentrations and similar finding were observed in Mediterranean and other fish species (Drosinos & Nychas, 1996;

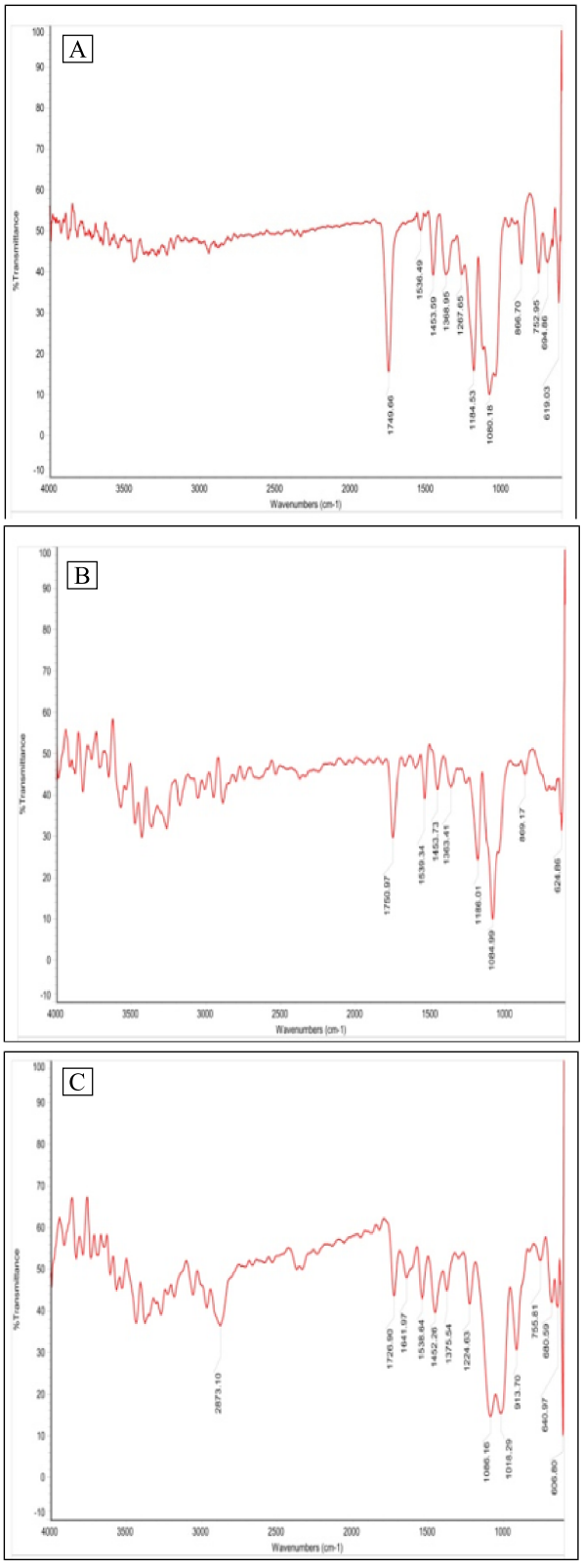

Fig. 4. FTIR spectrum, (A) Neat PLA (B) PLA / 1% NC (C) PLA / 2% NC

Dalgaard et al., 1997; Drosinos et al., 1997). In this study, the TMA value of all the samples were under acceptable limit of 10–15 mg 100 g^{-1} for human consumption (Connell, 1975).

The peroxide values increased progressively with storage period (Fig. 5D) and showed the maximum value of 10.48 ± 0.05 milli equivalents kg^{-1} on 20th day of storage for neat PLA samples. The initial PV value for the samples packed in PLA/NC 1%, 2%, 3%, Neat PLA & LDPE films, was 1.80± 0.24 equivalents kg^{-1} and increased to 9.70±0.24, 9.70±0.65, 9.68±0.20, 10.48±0.14, 10.25±0.04 milli equivalents kg^{-1} respectively on final day of storage and showed that, the values were within the acceptability limit of 18-20 milli equivalents kg^{-1} of fish sample (Reay & Shewan, 1949).

The presence of free fatty acids is due to the oxidation and hydrolysis of lipids and may be converted into odorous volatiles (Lindsay, 1994). The initial FFA content of samples were 10.73 ± 0.24 mg% oleic acid and it gradually increased to a maximum value of 19.33 ± 0.04 mg% oleic acid on the final day of storage for samples packed in PLA films (Fig. 5E). In PLA/NC 1%, 2% and 3%, Neat PLA and LDPE packed samples the initial FFA content was 10.73 ± 0.24 mg% oleic acid and reached 19.06±1.24, 19.33± 0.00, 19.16±1.14, 20.08±00 and 19.06± 0.14 mg% oleic acid on the final day of the storage period. A little fluctuation was observed in the FFA content of all the samples, which gradually increased throughout the storage period.

Total plate count of iced anchovy packed in various films differed significantly during storage (Fig. 5F). The initial bacterial count of samples was 3.89 log cfu g^{-1}. But the count in the samples decreased significantly on 5th day of storage and ranged from 1.0 to 2.69 log cfu g^{-1}. This may be due to the exposure of cold environment, which retarted the bacterial growth. Then a gradual increase in count was observed that reached to a final value of 4.63, 2.69, 3.55, 5.24 and 2.53 log cfu g^{-1} for PLA /1%, 2% and 3% PLA/NC, neat PLA, and LDPE films. Overall the samples packed in the PLA/NC based films exhibited better protection to the fish and the TPC values were within the acceptable limits for fresh fish (ICMSF, 1986).

The fabrication of PLA films by incorporation of nanocellulose at three different levels (1-3%) as filler and the application of these films for chilled storage of anchovies was studied. Incorporation of 3% of

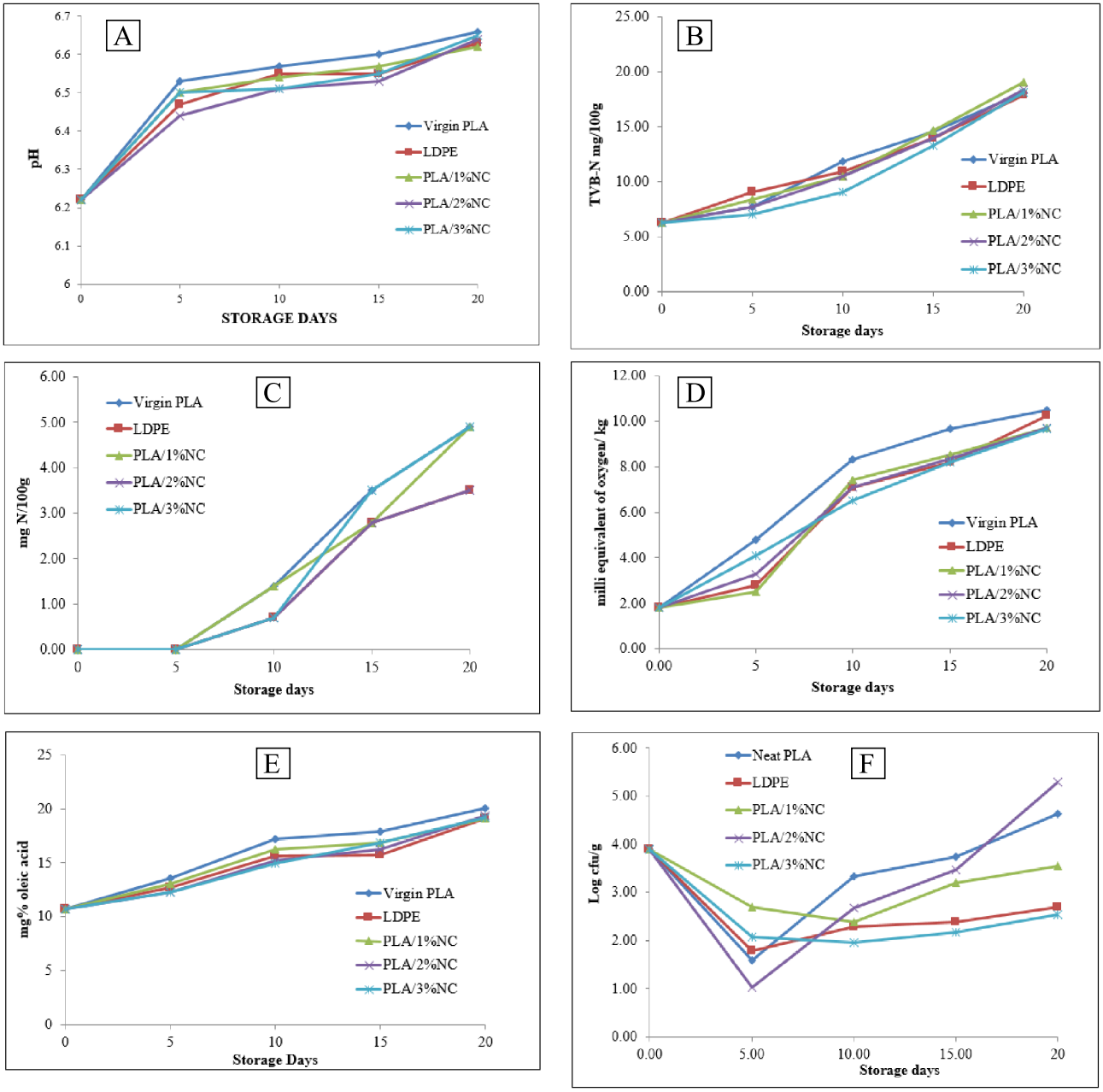

Fig. 5. Biochemical & Microbial changes during storage (A) pH (B) TVB-N (C) TMA (D) PV (E) FFA (F) TPC

nanocellulose in the PLA matrix enhanced the film forming properties of the films. The physical properties of the PLA films increased due to the addition of nanocellulose when compared to neat PLA films. The comparison with a commercial LDPE film determined that these films are comparable and could be used for the short-term preservation of chilled anchovy. PLA with 3% nanocellulose was suitable to prevent microbial growth and exhibit improved barrier properties up to 20 days of chilled storage. This study revealed that higher concentration of nanocellulose improved the mechanical properties of the film and retarded the spoilage of the anchovy during chilled storage.

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