



Development of High Oxygen Barrier Multi-layered Packaging Film for Shelf Life Extension of Ready-to-Cook (RTC) Idli Batter

P. S. Gaikwad¹, B. K. Yadav^{1*}, S. Anandakumar¹, M. Loganathan¹
and S. Shanmugasundaram¹

¹Indian Institute of Food Processing Technology, Ministry of Food Processing Industries, Government of India, Pudukkottai Road, Thanjavur - 613005, Tamil Nadu, India.

Authors' contributions

This work was carried out in collaboration among all authors. Author PSG designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors BKY and SA managed the analyses of the study. Authors ML and SS managed the literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IRJPAC/2020/v21i130146

Editor(s):

(1) Dr. Wolfgang Linert, Professor, Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt, Austria.

Reviewers:

(1) Vikramjit Kaur Zhawar, Punjab Agricultural University, India.
(2) Deepika Kohli, Maharana Pratap University of Agriculture and Technology, Udaipur, India.
Complete Peer review History: <http://www.sdiarticle4.com/review-history/54882>

Original Research Article

Received 07 December 2019
Accepted 14 February 2020
Published 18 February 2020

ABSTRACT

Aim: The current study focuses on development of high oxygen barrier multi-layered packaging film for shelf life extension of Ready-to-Cook (RTC) idli batter.

Place and Duration of Study: Department of Food Packaging and System Development at Indian Institute of Food Processing Technology, Thanjavur, Tamil Nadu, India, between Aug 2018 and Dec 2019.

Methodology: The developed multi-layered film composed with polypropylene (PP) nanocomposite by depositing silicon dioxide (SiO₂) on PP (0.010 mm) film and attached with different thickness of barrier layers were PP (0.010–0.053 mm) and ethylene-vinyl alcohol (EVOH 32%) film (0.066 mm) using layer-by-layer (LbL) process. The physical and chemical characteristics of commercial (A) and all developed multi-layered (B, C, D, E and F) films were tested for barrier and mechanical properties.

*Corresponding author: E-mail: binodkyadav@iifpt.edu.in;

Results and Discussion: The SEM analysis confirmed that the developed PP nanocomposite multi-layered films have a presence of SiO₂ with quasi-spherical structure with diameter ranging from 200 to 500 nm. FTIR analysis also identified the presence of Si-O-Si group on all the developed PP nanocomposite films at wavenumber ranges from 1100-900 cm⁻¹ and 467 cm⁻¹. The film composed with PP+SiO₂+EVOH (sample F) showed lower in oxygen transmission rate (OTR) of 452.46±33.94 cc/m²/24h and water vapour transmission rate (WVTR) of 1.07±0.16 g/m² day. The batter stored in sample F film help to extend the shelf life upto 33 h at ambient temperature and commercially stored batter spoiled quickly (24 h) at ambient temperature.

Keywords: PP nanocomposite; silicon dioxide; ethylene–vinyl alcohol; layer-by-layer; oxygen barrier.

ABBREVIATIONS

Differential Scanning Calorimetry (DSC); End set melt temperature (T_e); Enthalpy (ΔH_m); Fourier Transform Infrared Spectroscopy (FTIR); Glass transition temperature (T_g); Hour (h); Kilovolt (kV); Layer-by-layer (LbL); Melt peak temperature (T_m); Onset temperature (T_o); Oxygen Transmission Rate (OTR); Scanning Electron Microscopy (SEM); Sec (S); Silicon Dioxide (SiO₂); Universal Testing Machine (UTM); Water Vapor Transmission Rate (WVTR).

1. INTRODUCTION

Idli is a popular breakfast food item consumed all over India, Sri Lanka, Malaysia and Singapore [1,2]. Ready-to-Cook (RTC) packaged idli batter has a very short shelf life due to the presence of high moisture and live fermentation [1]. In India, there is a huge demand for RTC packaged idli batter with moderate shelf life and nowadays there are few non-thermal preservation techniques are utilized for extending the shelf life of RTC packaged idli batter [3-5]. Those non-thermal techniques are not viable and it coagulates RTC packaged idli batter due to heat. Nowadays consumer demand is growing towards fresh idli batter, hence there is a need to establish a new technique which can help to extend the shelf life of RTC packaged idli batter without coagulating it. There are certain innovative packaging technologies available for extending the shelf life of packaged food products but the main problem of food product spoilage is due to the poor barrier properties of packaging films and that can be improved with the help of multi-layered packaging films.

Polypropylene (PP) polymer belongs to polyolefins group ((C₃H₆)_n) and mostly used for food packaging application due to its lowest manufacturing cost available in the market till now [6]. Other most common used polymers for packaging application are polyethylene terephthalate, polystyrene, polyvinyl chloride and polyvinylidene [7]. PP is a thermoplastic polymer with low density (0.9 g/cm³), semi-crystalline, strong and light in weight [8]. PP films are a suitable and good choice for packaging

application due to its higher melting temperature (165°C), thermal stability, hardness, tensile strength and stiffness. PP polymers exhibit poor gas barrier properties due to poor molecular structure of polyolefins (CH₂ = CHR), which increases oxygen permeability and water vapour permeability of PP films [6,9,10]. There is a trend in utilizing the barrier properties of packaging films are improved with the help of nanocomposite material depositing on packaging films [11-15].

There is limitation to develop PP based nanocomposite film due to poor dispersion of nanocomposite materials. The compatibility between two materials such as nanocomposite material and polymer can be improved with the help of casting method. Nowadays, several casting methods are utilized to coat the packaging film using blade casting, dip casting, drop-casting, zone casting and vertical drying [16]. According to Modarres et al. [16], drop-casting is a suitable method for the casting of nanocomposite material on packaging film, because it can coat large area, control over droplet size, simple and low-cost process.

The SiO₂ is known as a safe and stable food additive for the preservation of foods. Nowadays, SiO₂ composite packaging films are used in the food and pharmaceutical industry due to its unique properties like high oxygen barrier, gas diffusion, durability, specific surface area and thermal stability and it can also be used as a replacement of aluminium films [13]. The strength of SiO₂ composite packaging film depends on the cohesive strength and adhesion

to the polymer and it can be improved using thumb rule, with an increase in the adhesion to the polymer or decrease in the thickness [17,18]. The coating of SiO₂ on packaging film increases the polymer crystallinity due to the increase in heat treatment (120°C) and resulted in higher interfacial strength [18]. According to Kim and Cha [19], packaging film developed with nanocomposite material has micro-crack problems. To address this problem, nanocomposite film was attached with barrier film on polyolefin foams [10]. The barrier layer attached with PP nanocomposite film shows poor adhesion with polyolefin foams and it can be improved using suitable adhesive in the appropriate amount to bind the two layers otherwise, there will be a chance of adhesive migration into the product with contact of packaging film [10,20].

The EVOH (C₂H₄O – C₂H₄)_x copolymer films are extensively used in the food industry due to its strong barrier properties against the oxygen. The EVOH copolymer composed with ethylene (20 to 60 mol%) produces flexibility and processability to the film and vinyl alcohol controls the barrier properties of the film [21]. EVOH copolymer is more popular in multilayer packaging industry for its lowest oxygen permeability rate due to the presence of small gaps in between the molecules. The barrier properties of EVOH against oxygen decreases as ethylene content increases and increase the vinyl content which decreases the moisture resistance [9]. EVOH copolymer also shows excellent barrier properties against carbon dioxide and nitrogen [21].

Commercially, multi-layered packaging films are developed through surface modification using electron beam evaporation, electrostatic deposition, plasma deposition, plasma treatment magnetron sputtering, polymeric composites sandwiching, polymerization, electrohydrodynamic and vacuum deposition [22-24]. These techniques are costlier and not easily available, but advantages obtained from the above methods can also be achieved through layer-by-layer (LbL) process. Azlin-Hasim et al. [25] reported that LbL disposition of polyethyleneimine and poly (acrylic acid) polymer with silver on UV/ozone treated LDPE film improve the antimicrobial activity against *Pseudomonas fluorescens* and *Staphylococcus aureus*. Similarly, it was observed that multilayer LbL silk matrix of poly (acrylic acid) and poly (dimethyldiallylammonium chloride) fabricated

with silver nanoparticles (AgNPs) was effective against bacterial growth. The LbL coating of packaging materials will improve the optical properties, wettability, resistance to scratch and increase the barrier properties to protect the food against internal microbial growth and external atmosphere of the food products [9,26].

In this study an effort has been made to develop a high oxygen barrier multi-layered packaging film using PP nanocomposite film attached with different thickness of barrier layers to protect the RTC packaged idli batter from interdiffusion of gases and control the headspace gas concentration of inside package to extend the shelf life RTC packaged idli batter.

2. MATERIALS AND METHODS

2.1 Materials and Chemicals

EVOH resin (32% of ethylene content) was provided by Kuraray Co., Ltd. (Tokyo, Japan) and other required chemicals used for this study were procured from Merck, Sigma, (Chennai, Tamil Nadu, India). All the materials in this study were used without further purification.

2.2 Development of PP Nanocomposite Film

The PP nanocomposite film was composed with SiO₂ on PP film with the help of drop-casting method as previously described by Modarres et al. [16], and the process of drop-casting was slightly modified by attaching a needle at the bottom of dropper to deliver very minute droplet of SiO₂ into nano size (Fig. 1). The SiO₂ nanoparticles of 100 nm were drop-casted on PP film of size 140 X 150 mm and dried at 60°C in the electrical drier (Model no. HK-0524 TRESS, Industrial and laboratory tools corporation, Chennai, India).

2.3 Development of PP Nanocomposite Multi-layered Packaging Film

Five different thickness of multi-layered packaging films was developed using PP (0.010 - 0.063 mm) and EVOH 32% (0.076 mm) films as summarized in Table 1. The developed PP nanocomposite (0.010 mm) film was attached with different thickness of barrier layers using acrylic acid as an adhesive. The developed multi-layered packaging films composed of two layers. The inner layer (PP nanocomposite) of multi-

layered packaging film was light transparent and resistant to water and gas. The outer layer (PP or EVOH) was used as a gas barrier and attached with 5% of acrylic acid. Later all the developed films with different thickness of barrier layers were dried at ambient condition ($32\pm 2^\circ\text{C}$) for three days [27]. The developed PP nanocomposite multi-layered packaging films were cut into the desired size (140 X 150 mm) and made into pouches with proper sealing of edges (Fig. 2). All the developed PP nanocomposite multi-layered films and commercial film were tested for structural, chemical, thermal, barrier and mechanical properties using standard procedure such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Oxygen Transmission Rate (OTR), Water Vapor Transmission Rate (WVTR), tensile and sealing strength.

2.4 Thickness Measurement of Commercial and PP Nanocomposite Films

The thickness of commercial and developed PP nanocomposite films was measured at different positions using a thickness tester (Serial no 547-401, Mitutoyo, Japan) and average value of the film was taken as a thickness of the film.

2.5 Morphological Characteristics of Commercial and PP Nanocomposite Films Using SEM Analysis

The microstructural characteristics of commercial and all PP nanocomposite multi-layered packaging films were analysed using SEM TESCAN, Model - Vega 3 (Kohoutovice, Czech Republic). The samples were prepared by cutting (20 X 20 mm) small strip of all the packaging films and mounted on the specimen holder using double side conductivity tape. The sample coating was done with gold-palladium to a thickness of about 100 Å for 30 S using vacuum evaporator for artificial conductance. The SEM analysis was operated at 10 kV with a magnification of 15,000 X.

2.6 Intermolecular Interaction of Commercial and PP Nanocomposite Films Using FTIR Spectroscopy

The surface coating and changes in functional groups made by SiO_2 on all PP nanocomposite multi-layered packaging films were analysed using spectrum two FTIR, Spectrophotometer, (PerkinElmer, USA). The samples were directly mounted on a sample holder and the spectra of all the films were recorded on the wavenumber ranges from $400\text{-}4000\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} with 12 scans [28].

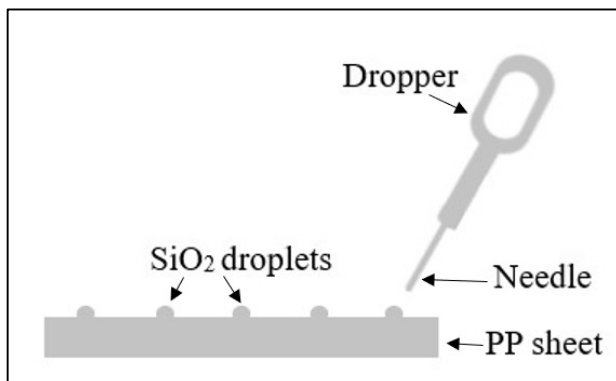


Fig. 1. Drop casting method tested to coat SiO_2 on PP sheet

Table 1. Different combination of polymer and thickness of packaging films

Packaging samples	Packaging materials	Barrier layer thickness (mm)	Outer layer thickness(mm)	Total thickness (mm)
A	PP (commercial)	0.010 mm	-	0.010 mm
B	PP+ SiO_2	0.010 mm (PP)	100 nm (SiO_2)	0.010 mm
C	PP+ SiO_2 +PP	0.010 mm (PP+ SiO_2)	0.023 mm (PP)	0.033 mm
D	PP+ SiO_2 +PP	0.010 mm (PP+ SiO_2)	0.033 mm (PP)	0.043 mm
E	PP+ SiO_2 +PP	0.010 mm (PP+ SiO_2)	0.053 mm (PP)	0.063 mm
F	PP+ SiO_2 +EVOH	0.010 mm (PP+ SiO_2)	0.066 mm (EVOH)	0.076 mm

Table 2. Determination of functional group for commercial (A) and PP nanocomposite multi-layered packaging films (B, C, D, E and F) using FTIR analysis

Sr. No.	Functional group	Molecular motion	Wavenumber (cm ⁻¹) with sample codes					
			A	B	C	D	E	F
1.	Alcohol	O-H (stretch)	3646	3649	3608	3607	3618	3654
2.	Amine	N-H (stretch)	3421	3441	3454	3464	3467	3434
3.	Alkane	C-H (stretch)	2916	2918	2918	2918	2918	2918
4.	Aldehyde	C=O (stretch)	1741	1741	1721	1741	1721	1721
5.	Alkane	-C-H (bending)	1455	1455	1463	1455	1455	1463
6.	Alkane	-C-H (bending)	1376	1376	1377	1376	1376	1367
7.	Ether	C-O (stretch)	1168	1167	1166	1167	1168	1196
8.	Ether	C-O (stretch)	1103	1103	1105	1103	1101	1102
9.	Silicon dioxide	Si-O-Si (stretch)	-	973.3	967.6	973.3	973.3	965
10.	Alkene	=C-H (bending)	841.3	841.6	718.9	841.7	841.7	840
11.	Alkene	=C-H (bending)	719	-	-	-	-	-
12.	Alkene	=C-H (bending)	696.8	-	-	-	-	-
13.	Alkyl halide	C-Br (stretch)	514.2	559.3	514.2	537.2	525.7	508.9
14.	Silicon dioxide	Si-O-Si (stretch)	-	467.5	467.3	468.9	467.8	467

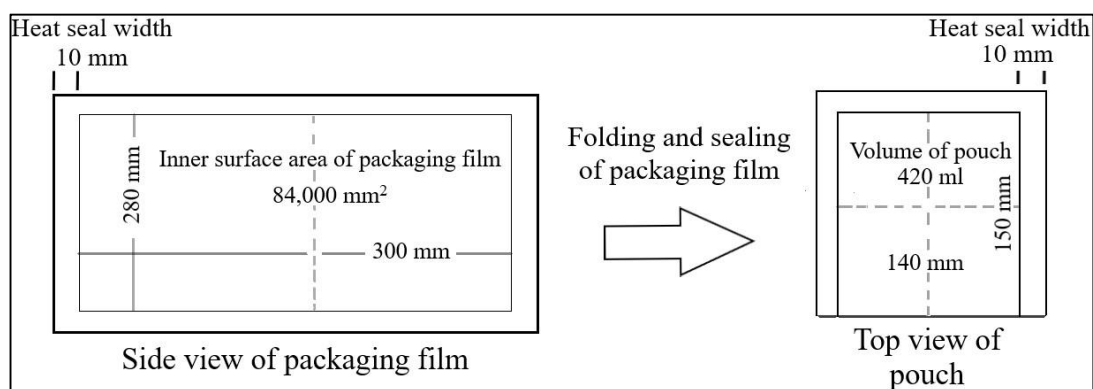


Fig. 2. Development of PP nanocomposite multi-layered (PP/SiO₂/adhesive/barrier layer) pouch for food packaging application

2.7 Thermal Properties of Commercial and PP Nanocomposite Films Using DSC

The DSC-7 Model (Perkin - Elmer) was used to identify the thermal properties of all PP nanocomposite multi-layered packaging films. All the films were cut into circular pieces and about 10 mg of mass was used for DSC analysis [28]. The cut samples were placed into the small discs having a diameter of 7 mm and covered with a lid diameter of 6.8 mm. The discs were pressed with the help of aluminium pans to avoid the external air and adsorption of moisture. The reference sample was an empty disc. The temperature range was selected according to Sudhamani et al. [28], which ranges from 40 to 200°C and the heating/cooling rate was 10°C min⁻¹. All the developed samples run was performed under nitrogen flow at 20 cm³min⁻¹. The changes in temperature and enthalpy were determined with standard Indium using thermal software version 5.42. The characteristics of the polymer used in multilayer packaging were presented in Table 2.

2.8 Oxygen Permeability of Commercial and PP Nanocomposite Films Using OTR

The oxygen permeability of commercial and all PP nanocomposite multi-layered packaging films were carried out using OX-TRAN OTR, model no 2/12 (MOCON, Minneapolis, MN, USA). Measurement conditions were 23°C and 0% relative humidity (RH) at 1 atm in compliance with ASTM D-3985. Each film was measured for different places and the average of measurements was taken for all the sample (cc/(m².day.atm)).

2.9 Water Vapour Permeability of Commercial and PP Nanocomposite Films Using WVTR

The WVTR value of commercial and all PP nanocomposite multi-layered packaging films were carried out using Water Vapor Permeation Analyzer, Model Lyssy L80-5000 (Illinois Instruments, Johnsburg, USA) according to the standard procedure of ASTM F-1249. Measurement conditions were 37°C and a gradient of 90% RH. The average of measurements was taken for all the samples (g/m².day).

2.10 Mechanical Properties of Commercial and PP Nanocomposite Films Using UTM

The tensile and heat seal strength of commercial and all PP nanocomposite multi-layered packaging films were analyzed using UTM (Pack Test KC-3000; 100 N load cell). All the packaging films were cut into 100 mm X 25 mm and tested at a crosshead speed of 100 mm/min. The tensile strength of each sample was carried out by ASTM D-638 standard procedure and heat seal strength for all the samples were done by ASTM F-88 standard procedure.

2.11 Shelf Life Extension of RTC Packaged Idli Batter

2.11.1 Preparation of idli batter and storage condition

Parboiled rice (*Oryza sativa*) and black gram (*Phaseolus mungo*) dhal were procured from the local market of Thanjavur (Tamil Nadu, India)

and soaked separately for 4-6 h. After that water was drained out and grounded separately with the occasional addition of water at 1.5 to 2.0 times of the initial weight. Idli batter was prepared with 3:1 blend ratio of rice to black gram dhal and mixed with 2% of salt [2,29]. The 150 g of fresh idli batter was packed into commercial and developed PP nanocomposite multi-layered packaging film to determine the shelf life of packaged idli batter at ambient temperature. The packaged idli batter was allowed for different fermentation time and periodically analyzed (every 1 h of intervals) for headspace gas analysis (CO_2) up to the spoilage of idli batter at ambient condition.

2.11.2 Headspace gas analysis for monitoring shelf life of packaged idli batter

The headspace gas concentration of packaged idli batter was monitored using headspace gas analyser (Serial no. 87131699, CheckMate3, Dansensor, Denmark) to determine the shelf life of packaged idli batter at ambient temperature.

2.12 Statistical Analysis

All the experimental data were analysed statistically, non-linear analysis was performed using Microsoft Excel 2019 (Microsoft Corp., Redmond, WA, USA) for Windows 10.0.

3. RESULTS AND DISCUSSION

3.1 Development of Suitable Packaging Material for RTC Packaged Idli Batter

A total of five types of high barrier PP nanocomposite packaging film was developed, namely, PP+ SiO_2 (0.010 mm), PP+ SiO_2 +PP (0.033 mm), PP+ SiO_2 +PP (0.043 mm), PP+ SiO_2 +PP (0.063 mm) and PP+ SiO_2 +EVOH (0.076 mm). The thickness of packaging materials ranges from 0.010 to 0.076 mm. All the developed packaging films were tested for the barrier properties and physical strength and results were described as follows.

3.2 SEM Analysis of Developed PP Nanocomposite Multi-layered Films as Compared to Commercial Film

The SEM images of the developed films are shown in Fig. 3. The PP nanocomposite packaging films showed a quasi-spherical structure with diameter ranging from about 200-500 nm with a polymer background (Fig. 3. B, C,

D, E, and F) and similar results were also observed by Li et al. [11] for the microencapsulated paraffin SiO_2 . Thus, SEM images revealed that all developed PP nanocomposite packaging films using drop-casting method possess SiO_2 as intended (Fig. 3).

3.3 Intermolecular Interaction of Commercial and PP Nanocomposite Packaging Films Using FTIR Spectroscopy

The presence of SiO_2 and changes made by SiO_2 on the surface of developed PP nanocomposite packaging films were characterized using FTIR spectra shown in Fig. 4. Table 2 summarizes the major functional group present in all the packaging material tested. It is obvious from the Table 2 that major functional group, namely, alcohol, amine, alkane, aldehyde, alkane, ether and alkyl halide are present in commercial and developed PP nanocomposite packaging films. The stretching of O-H (alcohol) group showed peak at 3654 cm^{-1} for sample F (PP+ SiO_2 +EVOH) film and packaging film A, B, C, D and E showed stretching of O-H group on wavenumber ranges from 3607 to 3646 cm^{-1} (Table 2). The hydroxyl group (amines) showed stretching of N-H group at 3434 cm^{-1} for sample F film while the commercial (A) film it was observed on peak at 3421 cm^{-1} . The stretching of N-H group of sample B, C, D and E were observed on wavenumber ranges from 3441 to 3467 cm^{-1} (Table 2). However, the functional groups of amines were also recorded on these peaks and results confirmed that silica contains enough amines. The stretching of C=O (aldehyde) bond on commercial and PP nanocomposite packaging films were observed on wavenumber between 1721 to 1741 cm^{-1} . All the PP nanocomposite packaging films (B, C, D, E and F) showed stretching of C-H (alkane) bond on wavenumber at 2918 cm^{-1} and commercial film showed peak at 2916 cm^{-1} . The deformation of $-\text{CH}_3$ and $-\text{CH}_2$ groups were observed peak at 1370 to 1470 cm^{-1} and stretching of C-O (ether) group was observed on band ranges from 1101 to 1300 cm^{-1} in all the packaging films. The bending of =C-H (alkene) group was observed on wavenumber ranges from 675 to 900 cm^{-1} for commercial and PP nanocomposite packaging films. The stretching of C-Br (alkyl halide) group was observed for commercial and all developed PP nanocomposite packaging film on the wavenumber ranges from 500 to 600 cm^{-1} .

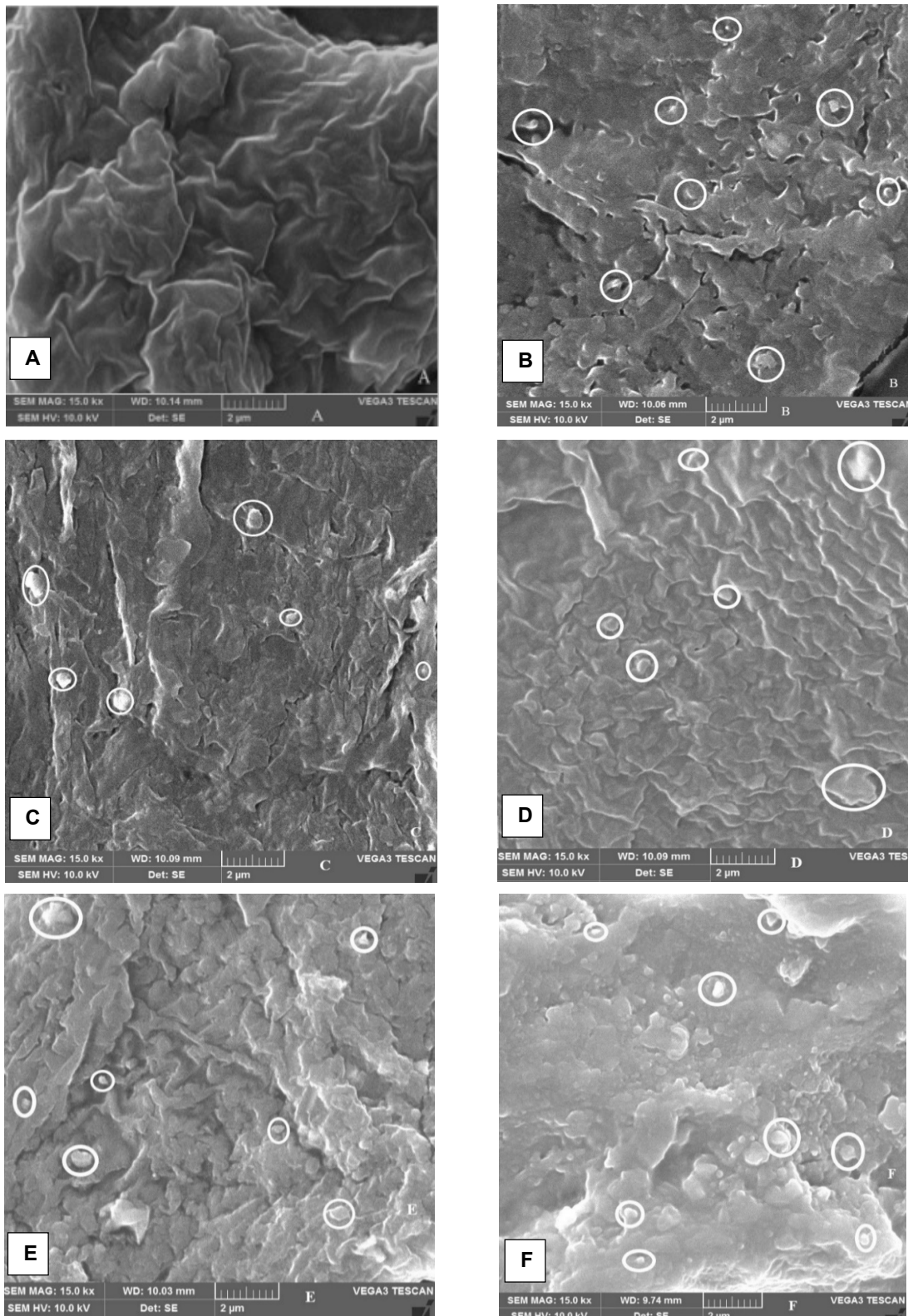


Fig. 3. SEM images of commercial (A) and PP nanocomposite multi-layered packaging films (B, C, D, E and F)

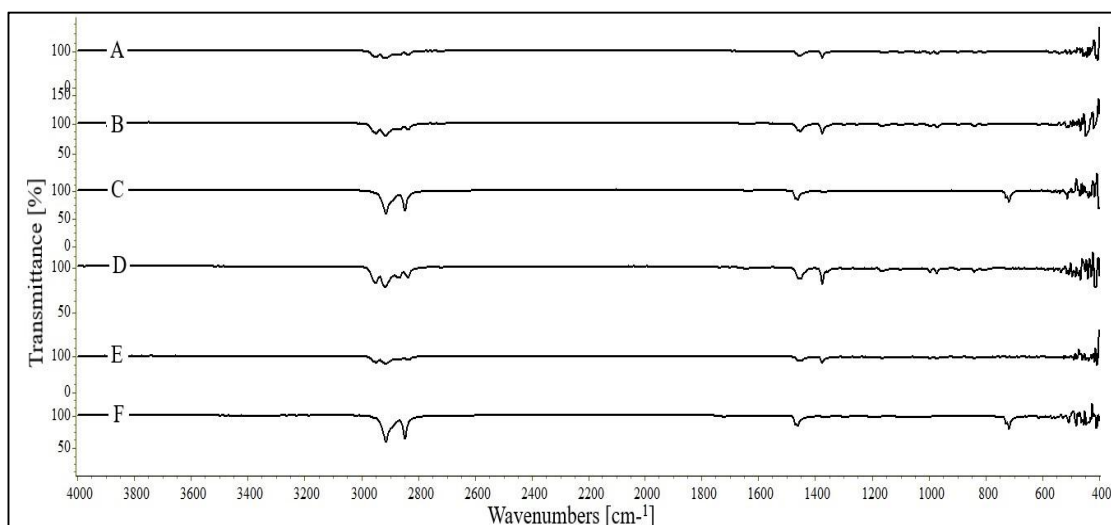


Fig. 4. FTIR spectra of commercial (A) and PP nanocomposite multi-layered packaging films (B, C, D, E and F)

Table 3. Thermal characteristics of commercial (A) and PP nanocomposite multi-layered packaging films (B, C, D, E and F) analyzed using DSC

Packaging samples	T_g	T_o	T_m	T_c	Range (T_c-T_o)	ΔH_m (Jg ⁻¹)
A	-11.23	150.08	164.15	172.09	22.01	233.31
B	0.54	150.57	165.47	173.51	22.94	247.85
C	1.46	151.26	165.73	173.70	22.44	262.38
D	1.46	151.81	165.81	174.36	22.55	330.24
E	1.46	152.50	165.99	174.97	22.47	343.46
F	1.48	153.95	166.45	175.08	21.13	350.68

The extra peaks on PP nanocomposite packaging films was attributed to Si-O-Si (silicon dioxide) group on band ranges from 1100-900 cm^{-1} and 467 cm^{-1} [30-32] and similar results were found on all the developed PP nanocomposite packaging (B, C, D, E and F) films (Table 2). No more additional peaks were observed on commercial and PP nanocomposite packaging films. The FTIR analysis confirmed that all the developed PP nanocomposite packaging films has a presence of Si-O-Si group and there were no more chemical changes observed during the coating of SiO_2 on PP films.

3.4 Thermal Properties of Commercial and PP Nanocomposite Packaging Films Using DSC

The parameters of thermal characteristics of commercial and developed PP nanocomposite

packaging films characterized using DSC are mentioned in Table 3. The commercial film showed T_g at -11.23°C which was below the ambient temperature while the sample F film showed higher T_g value at 1.48°C . The film developed with sample C, D and E showed single T_g at 1.46°C (Table 3).

The heating of two or more polymers (PP+ SiO_2 or PP+ SiO_2 +PP or PP+ SiO_2 +EVOH) with different blend ratios generate separate peaks on DSC thermograms as depicted in Fig. 5. The temperature equivalent to the peak temperature denotes as a melt peak temperature (T_m). The commercial film (sample A) showed the lowest T_m at 164.15°C and developed PP nanocomposite films B, C, D, E and F showed slightly higher T_m respectively, at 166.45 , 165.47 , 165.73 , 165.81 , 165.99 and 166.45°C which was due to interactions between two or more polymers.

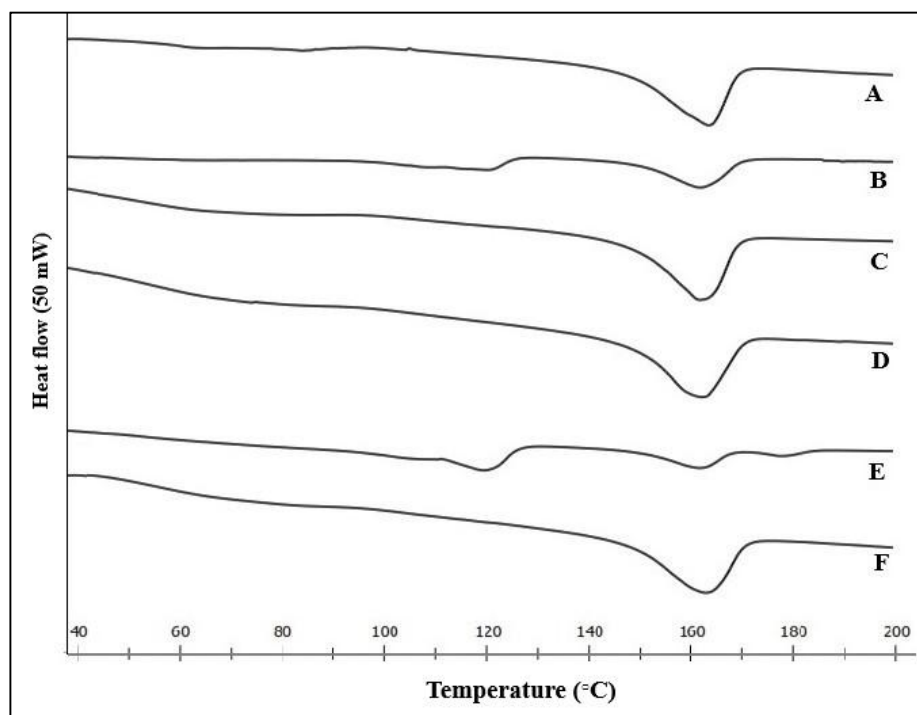


Fig. 5. DSC thermograms of commercial (A) and PP nanocomposite multi-layered packaging films (B, C, D, E and F)

From Fig. 5, it was observed that the developed PP nanocomposite films showed endothermic peak and it was well correlated with the melting of polymers. The developed packaging film B and E showed three peaks (Fig. 5). The first and second peak on sample B film was observed at 95°C and 121°C and for sample E film it was observed at 125°C and 182°C. The third peak for sample B and E showed constant single peak at 164°C which corresponds to PP polymer. According to Li et al. [33], the presence of three peaks is due to the presence of different molecules or polymers.

The difference between completion melt temperatures (T_c) and onset temperature (T_o) for all the developed PP nanocomposite films varies from 21.13 to 22.94°C and commercial film (A) showed a difference of 22.01°C. The enthalpy values of commercial film (A) was 233.31 Jg⁻¹ and the corresponding values for developed PP nanocomposite, namely, B, C, D, E and F were respectively, 247.85, 262.38, 330.24, 343.46 and 350.68 Jg⁻¹. The enthalpy (ΔH_m) of developed PP nanocomposite film was found to be higher as compared to the commercial film.

The results obtained by thermograms indicated that there was a variation in thermal stability as

indicated by variation in ΔH_m value. The variation was due to the barrier layer used for the preparation of PP nanocomposite packaging films. According to Becaro et al. [32] and Li et al. [33], the use of nanocomposite material (SiO₂) in the packaging film helps to increase the thermal stability of the developed packaging film and increase in the content of nanocomposite material or thickness of packaging film provides higher heat diffusion which delays the burning of materials due to grafting reaction within two or more polymers.

3.5 Oxygen Permeability of Commercial and PP Nanocomposite Packaging Films Using OTR

The OTR values of commercial and PP nanocomposite packaging films were presented in Fig. 6. The OTR value for commercial film was 1274.57±155.25 cc/m²/24h. The corresponding values for developed PP nanocomposite films were respectively, 1261.94±153.71, 781.81±73.22, 665.90±58.19, 517.837±40.80 and 452.46±33.94 cc/m²/24h for B, C, D, E and F samples. From the Fig. 6 it was observed that the sample A and B, C and D, D and E and E and F were not significantly different from each other.

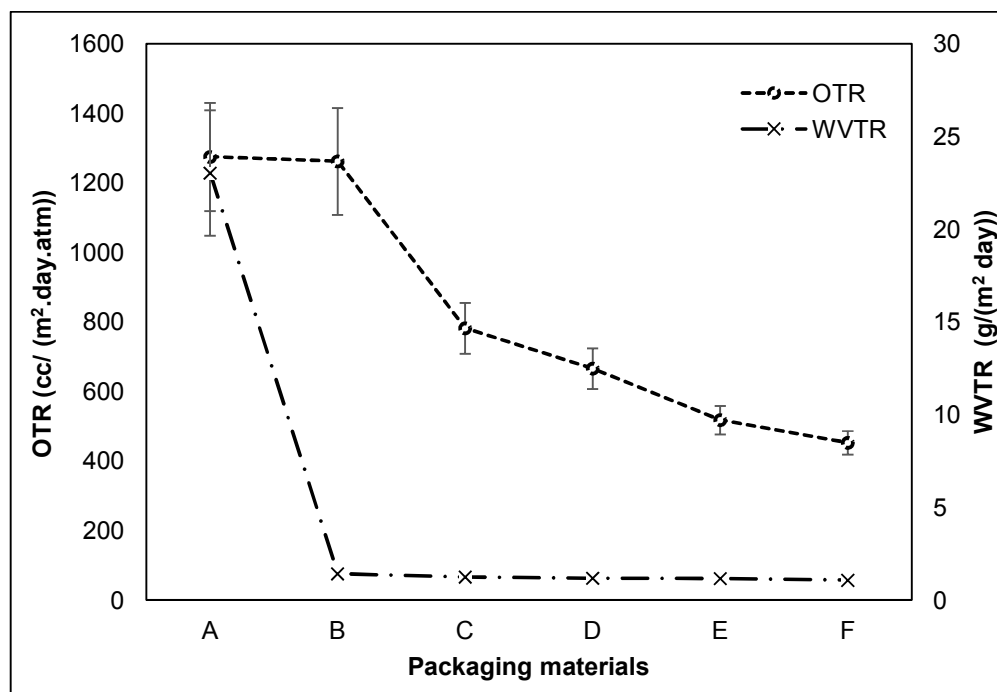


Fig. 6. OTR and WVTR values of commercial (A) and PP nanocomposite packaging films (B, C, D, E and F)

The commercial film showed higher OTR value as compared to PP nanocomposite films and lower OTR value was observed for sample F film. From Fig. 4 it was obvious that the OTR value of developed PP nanocomposite films was found to be decreased with the increased in the thickness of barrier layer (PP/EVOH), it was due to the presence of small gaps in between the molecules which decreases the value of OTR and similar results were also observed by Maes et al. [21].

3.6 Water Vapor Permeability of Commercial and PP Nanocomposite Packaging Films Using WVTR

The WVTR analysis was carried out to determine the permeability and diffusivity of commercial and PP nanocomposite packaging films and results are depicted in Fig. 6. The WVTR value of the commercial film was found to be higher (23.03 ± 3.38 g/m²·day) as compared to developed PP nanocomposite packaging films which were respectively, 1.42 ± 0.21 , 1.24 ± 0.19 , 1.18 ± 0.17 , 1.16 ± 0.18 and 1.07 ± 0.16 g/m²·day for B, C, D, E and F samples. From the Fig. 6 it was observed that the sample B, C, D, E and F were not significantly different from each other. However, sample A was significantly different from other samples. The developed PP nanocomposite films showed lower in WVTR

value as compared to commercial film due to the densification and void diminution which helps to lower the WVTR value. Similar results were also observed by Bieder et al. [34] for the SiO₂ diffusion barriers on flexible packaging materials.

3.7 Mechanical Properties of Commercial and PP Nanocomposite Packaging Films Using UTM

The tensile strength of commercial and PP nanocomposite films calculated using UTM are shown in Fig. 7. The tensile strength value for commercial film was found to be 34.77 ± 1.20 MPa. The corresponding values for developed PP nanocomposite films were respectively, 33.30 ± 1.01 , 34.89 ± 1.00 , 34.71 ± 0.77 , 34.52 ± 0.46 and 35.89 ± 0.55 MPa for sample B, C, D, E and F films. The sample B showed lower tensile strength as compared to commercial film which was due to the crack formation on the film created by the deposited nanocomposite material such as SiO₂ and similar results were also observed by other researchers [19,30]. From the Fig. 7 it was observed that the sample A, B, C, D and E were not significantly different from each other. However, sample F was significantly different from sample A and B. The higher value of sample F might be due to the EVOH which is a tougher material as compared to PP [10].

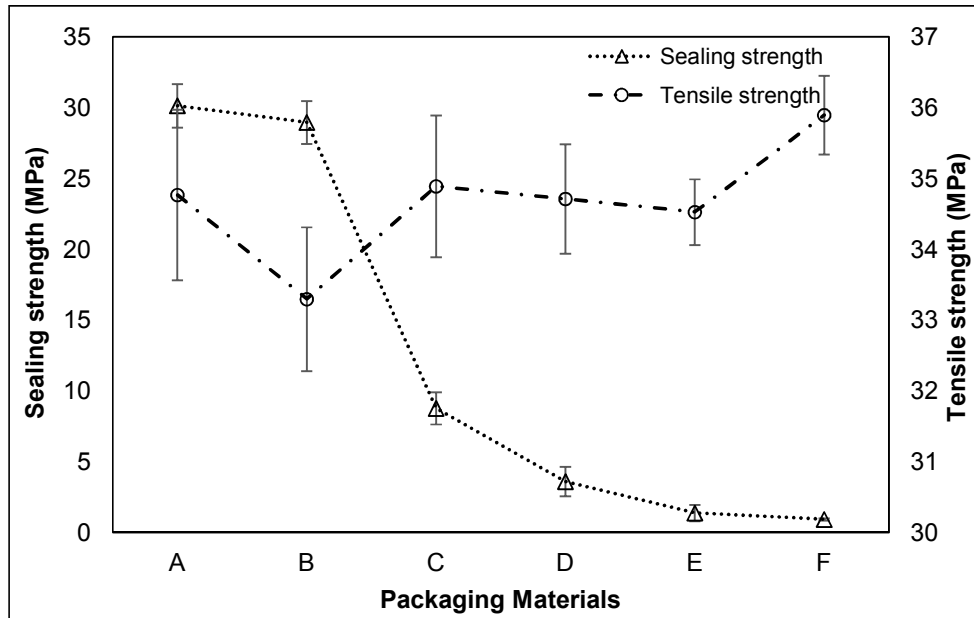


Fig. 7. Tensile and sealing strength of commercial (A) and PP nanocomposite packaging films (B, C, D, E and F)

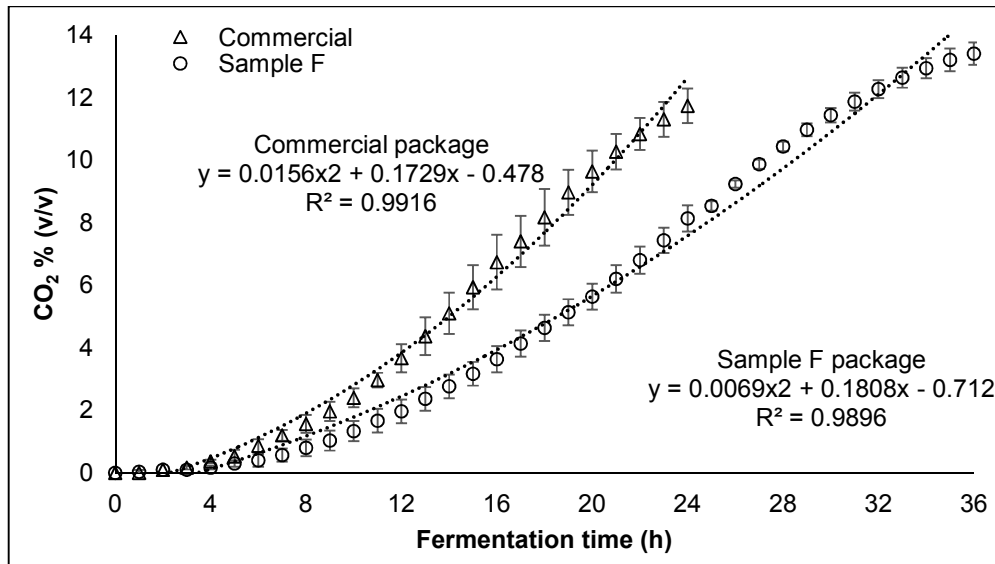


Fig. 8. CO₂ concentration of headspace of packaged idli batter with respect to storage (fermentation) time at ambient temperature

3.8 Tensile and Sealing Strength of Commercial and PP Nanocomposite Packaging Films

The results of heat-seal strength for commercial and PP nanocomposite packaging films are shown in Fig. 7. The heat-seal strength value for commercial film was found to be 30.13±1.53 MPa. The corresponding values for developed

PP nanocomposite films were respectively, 28.96±1.51, 8.77±1.13, 3.60±1.04, 1.38±0.57 and 0.93±0.07 MPa for sample B, C, D, E and F films. The PP nanocomposite film (B) showed slightly lower in heat-seal strength as compared to the commercial film which was due to the presence of crack formation during deposition of SiO₂. From the Fig. 7 it was observed that the sample A and B, and E and F were not

significantly different from each other. However, sample C and D was significantly different from each sample.

The developed PP nanocomposite multi-layered films (C, D, E and F) showed lower in heat-seal strength due to increase in the thickness of the barrier layer (PP/EVOH), presence of adhesive and air gaps in between the two layers of multi-layered films. According to Cheung [35], the sealing strength of the multi-layered packaging film can be improved using zip-lock packaging system.

From the above result it was observed that the developed PP nanocomposite multi-layered packaging film with sample F (PP+SiO₂+EVOH) showed lower in OTR and WVTR values, and higher in thermal stability and tensile strength. Hence, it was decided to do further study using sample F film and compared it with available commercial packaging film to determine the shelf life of stored batter with headspace gas concentration at ambient temperature.

3.9 Shelf Life Extension of Packaged Idli Batter

The concentration of CO₂ (% v/v) present into the headspace of RTC packaged idli batter are shown in Fig. 8. The CO₂ concentration into the headspace of commercial film ranged from 0 to 11.73±0.55% and in sample F film it ranged from 0 to 13.40±0.36%. The CO₂ concentration into the headspace of packaged batter started increasing from 0 % (v/v) and it increases rapidly upto the optimum level and later steady increase was observed which was due to increase in acidity content [29]. From Fig. 8 it was observed that the batter stored in commercial film spoiled at 24 h and batter stored in sample F film spoiled at 36 h at ambient temperature. The batter stored in sample F help to extend the shelf life of RTC idli batter upto the 33 h which was due to its higher barrier properties helped to slow down the growth of microbes. In sample F film, the amount of O₂ concentration is fixed inside the package and later it was utilized for respiration (CO₂). Sample F film helps to multiply the bacteria till optimum count and help to increase the CO₂ concentration at slow rate (Fig. 8). According to Winotapun et al. [36], the CO₂ concentration present in the headspace of the package depends on the properties of packaging film (OTR, WVTR, headspace volume and storage condition) and quality of food product (respiration rate) to be stored.

The variation in CO₂ concentration of stored batter in commercial as well as developed PP nanocomposite film (F) showed non-linear nature (2nd order polynomial equation) curve. The relationship can be expressed with the eq. 1.

$$\text{CO}_2 = at^2 - bt + c \quad (1)$$

Where,

$$\begin{aligned} a, b \text{ and } c &= \text{Constant} \\ t &= \text{Time} \end{aligned}$$

The values of a, b and c for commercially stored batter were 0.0156, 0.1729 and 0.478 for commercial film and the corresponding values of CO₂ concentration for batter stored in sample F was respectively, 0.0069, 0.1808 and 0.712 with an R² of 0.99. The CO₂ concentration of batter stored in commercial and F packaging film could estimate from storage duration which is evident from the close to unity slope (0.99) and high R² (0.99) value of the straight line fitted between actual and estimated values. From above result it was observed that PP nanocomposite film developed with sample F helps to extend the shelf life stored batter at ambient condition.

4. CONCLUSION

The developed high oxygen barrier multi-layered packaging films attached with different barrier layers of PP/EVOH films have been characterized with different techniques, including SEM, FTIR, DSC OTR, WVTR and mechanical strength. The SEM and FTIR analysis confirmed the presence of SiO₂ in all the developed PP nanocomposite multi-layered packaging films (sample B, C, D, E and F). FTIR analysis confirmed the presence of amine, alcohol, aldehyde, alkane and ether groups on developed PP nanocomposite multi-layered packaging films. DSC thermograms showed single T_g at 1.46°C for sample C, D and E and for sample F it was observed at 1.48°C. The T_m of developed PP nanocomposite films was found to be increased as increase in the thickness of the barrier layer. The OTR and WVTR values were found to be less in all PP nanocomposite multi-layered packaging film as compared to commercial film. The lower tensile strength was observed on sample B due to presence of micro-crack created by SiO₂ on all the PP nanocomposite film and higher tensile strength was observed on sample F due to EVOH is a tougher material. The heat-sealing strength for all the PP nanocomposite multi-layered films was found to be lower due to

the presence of adhesive and air gaps between the two layers. The film developed with sample F (PP/SiO₂/EVOH) showed better barrier and mechanical properties and help to extend the shelf life of packaged idli batter up to 33 h at ambient temperature.

ACKNOWLEDGEMENT

The financial assistance was provided by the Indian Institute of Food Processing Technology (IIFPT), Ministry of Food Processing Industries, Government of India, Thanjavur, Tamil Nadu, India, which is duly acknowledged.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Nisha P, Ananthanarayan L, Singhal RS. Effect of stabilizers on stabilization of idli (traditional South Indian food) batter during storage. *Food Hydrocoll.* 2005;19(2): 179-186.
- Sridevi J, Halami PM, Vijayendra SVN. Selection of starter cultures for idli batter fermentation and their effect on quality of idlis. *J. Food Sci. Technol.* 2010;47(5): 557-563.
- Ko JA, Kim WY, Park HJ. Effects of microencapsulated Allyl isothiocyanate (AITC) on the extension of the shelf-life of Kimchi. *Int. J. Food Microbiol.* 2012; 153(1-2):92-98.
- Chelliah R, Ramakrishnan SR, Premkumar D, Antony U. Bio-fortification and shelf-life extension of idli batter using curry leaves (*Murraya koenigii*). *J. Food Sci. Technol.* 2016;53(6):2851-2862.
- Mulmule MD, Shimmy SM, Bambole V, Jamdar SN, Rawat KP, Sarma KSS. Combination of electron beam irradiation and thermal treatment to enhance the shelf-life of traditional Indian fermented food (Idli). *Radiat. Phys. Chem.* 2017;131: 95-99.
- Yeo JH, Lee CH, Park CS, Lee KJ, Nam JD, Kim SW. Rheological, morphological, mechanical and barrier properties of PP/EVOH blends. *Adv. Polym. Tech.* 2001; 20(3):191-201.
- Vishnuvarthanan M, Rajeswari N. Effect of mechanical, barrier and adhesion properties on oxygen plasma surface modified PP. *Innov Food Sci. Emerg. Technol.* 2015;30:119-126.
- Meille SV, Ferro DR, Brückner S, Lovinger AJ, Padden FJ. Structure of beta-isotactic polypropylene: A long-standing structural puzzle. *Macromolecules.* 1994;27(9):2615-2622.
- Piergiovanni L, Limbo S. Food packaging materials. Springer. 2016;33-49.
- Feng J, Li Z, Olah A, Baer E. High oxygen barrier multilayer EVOH/LDPE film/foam. *J. Appl. Polym. Sci.* 2018;135(26):46425.
- Li J, Yang R, Yu J, Liu Y. Deterioration of polypropylene/ silicon dioxide nanocomposites before oxidative degradation. *J. Appl. Polym. Sci.* 2009;113(1):601-606.
- Körner L, Sonnenfeld A, Von Rohr PR. Silicon oxide diffusion barrier coatings on polypropylene. *Thin Solid Films* 2010; 518(17):4840-4846.
- Liu X, Chen X, Ren J, Chang M, He B, Zhang C. Effects of nano-ZnO and nano-SiO₂ particles on properties of PVA/xylan composite films. *Int. J. Biol. Macromol.* 2019;132:978-986.
- Hajibabazadeh S, Palahang M, Aghjeh MR. Effect of morphology development on mechanical properties and fracture behavior of PP/EPDM/SiO₂ blend-nanocomposites. *Polym. Test.* 2019;73:124-134.
- Jung BN, Kang D, Cheon S, Shim JK, Hwang SW. The addition effect of hollow glass microsphere on the dispersion behavior and physical properties of polypropylene/clay nanocomposites. *J. Appl. Polym. Sci.* 2019;136(14):47476.
- Modarres MH, Kosasih FU, Ducati C, De Volder M. Self-assembly of rGO coated nanorods into aligned thick films. *Adv. Mater Interfaces.* 2019;6(14):1900219.
- Felts JT. Transparent gas barrier technologies. *J. Plas. Film Sheet.* 1993; 9(3):201-223.
- Leterrier Y, Boogh L, Andersons J, Manson JA. Adhesion of silicon oxide layers on poly (ethylene terephthalate). I: Effect of substrate properties on coating's fragmentation process. *J. Polym. Sci. Pol. Phys.* 1997;35(9):1449-1461.
- Kim SW, Cha SH. Thermal, mechanical, and gas barrier properties of ethylene vinyl alcohol copolymer-based nanocomposites for food packaging films: Effects of nanoclay loading. *J. Appl. Polym. Sci.* 2014;131(11).

20. Félix JS, Isella F, Bosetti O, Nerín C. Analytical tools for identification of non-intentionally added substances (NIAS) coming from polyurethane adhesives in multilayer packaging materials and their migration into food simulants. *Anal. Bioanal. Chem.* 2012;403(10):2869-2882.
21. Maes C, Junior GMY, Teniers C, Luyten W, Herremans G, Peeters R, Samyan P, Carleer R, Buntinx M. Ethylene Vinyl Alcohol Copolymer (EVOH) as a functional barrier against surrogate components migrating from paperboard. *J. Chem.* 2019.
22. Kugel A, Staflien S, Chisholm BJ. Antimicrobial coatings produced by "tethering" biocides to the coating matrix. *Prog. Org. Coat.* 2011;72(3):222-252.
23. Kääriäinen T, Cameron D, Kääriäinen ML, Sherman A. Atomic layer deposition: Principles, characteristics, and nanotechnology applications. John Wiley & Sons; 2013.
24. Fabra MJ, López-Rubio A, Lagaron JM. Use of the electrohydrodynamic process to develop active/bioactive bilayer films for food packaging applications. *Food Hydrocoll.* 2016;55:11-18.
25. Azlin-Hasim S, Cruz-Romero MC, Cummins E, Kerry JP, Morris MA. The potential use of a layer-by-layer strategy to develop LDPE antimicrobial films coated with silver nanoparticles for packaging applications. *J. Colloid. Interface Sci.* 2016; 461:239-248.
26. Noshad M, Mohebbi M, Shahidi F, Koocheki A. Effect of layer-by-layer polyelectrolyte method on encapsulation of vanillin. *Int. J. Biol. Macromol.* 2015;81: 803-808.
27. Kim JM, Lee MH, Ko JA, Kang DH, Bae H, Park HJ. Influence of food with high moisture content on oxygen barrier property of polyvinyl alcohol (PVA)/ vermiculite nanocomposite coated multilayer packaging film. *J. Food Sci.* 2018;83(2):349-357.
28. Sudhamani SR, Prasad MS, Sankar KU. DSC and FTIR studies on gellan and polyvinyl alcohol (PVA) blend films. *Food Hydrocoll.* 2003;17(3):245-250.
29. Balasubramanian S, Viswanathan R. Properties of idli batter during its fermentation time. *J. Food Process. Pres.* 2007;31(1):32-40.
30. Deilmann M, Theiß S, Awakowicz P. Pulsed microwave plasma polymerization of silicon oxide films: Application of efficient permeation barriers on polyethylene terephthalate. *Surf. Coat. Technol.* 2008;202(10):1911-1917.
31. Jeziórska R, Świerz-Motysia B, Zielecka M, Szadkowska A, Studziński M. Structure and mechanical properties of low-density polyethylene/spherical silica nanocomposites prepared by melt mixing: The joint action of silica's size, functionality, and compatibilizer. *J. App. Polym. Sci.* 2012;125(6):4326-4337.
32. Becaro AA, Puti FC, Correa DS, Correa EC, Marconcini JM, Ferreira MD. Polyethylene films containing silver nanoparticles for applications in food packaging: Characterization of physico-chemical and anti-microbial properties. *J. Nanosci. Nanotechnol.* 2015;15(3):2148-2156.
33. Li B, Liu T, Hu L, Wang Y, Gao L. Fabrication and properties of microencapsulated paraffin@ SiO₂ phase change composite for thermal energy storage. *ACS Sustain Chem. Eng.* 2013; 1(3):374-380.
34. Bieder A, Gruniger A, Rudolf von Rohr R. Deposition of SiO_x diffusion barriers on flexible packaging materials by PECVD. *Surf. Coat. Technol.* 2005;200(1-4):928-931.
35. Cheung G. Zip lock. US, Patent No. 11/042,557; 2006.
36. Winotapun C, Phattarateera S, Aontee A, Junsook N, Daud W, Kerddonfag N, Chinsirikul W. Development of multilayer films with improved aroma barrier properties for durian packaging application. *Packag. Technol. Sci.* 2019;2 (8):405-418.

© 2020 Gaikwad et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
 The peer review history for this paper can be accessed here:
<http://www.sdiarticle4.com/review-history/54882>