Development and characterization of commercial biodegradable films using blown film extrusion technology

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The aim of this study was to develop commercial polylactic acid (PLA), PLA + polyethylene glycol (PEG) and PLA + polybutylene adipate terephthalate (PBAT)-based biodegradable films using blown film extrusion technology. The films produced were characterized for morphological, structural, optical, mechanical and thermal properties. The haze %, tensile strength, oxygen transmission rate (OTR), water vapour transmission rate (WVTR) parameters were varied from 10.65% to 28%, 48.3 to 56.49 MPa, 194.55 to 318.25 cc/m^2/day and 175 to 318.18 (gm/m^2/day) respectively for developed films. The study showed that better haze properties in biofilm are achived by compatibilizing with PEG. Thermal degradation of virgin PLA takes place in a single weight loss step with degradation peak at 349.77°C compared to PLA + PBAT blended that took two weight loss step. Fourier-transform infrared spectroscopy study was used to monitor the absorption peak shifts in specific regions to determine the known functional group interactions of the PLA with various types of materials. In all the films the absorbtion peaks appeared at 1451.2–1451.7 and 2921.2–2944.3 cm^{-1} corresponding to asymmetrical deformation of C–H bond. The stretching of C=O band vibration appeared at 1745.2–1745.7 cm^{-1} in PLA, PLA + PEG and PLA + PBAT film. From the fracture scanning electron microscope micrographs, there was smooth surface texture for films, and no interfacial differences were visible indicating the presence of a single phase and structural integrity of the films. The developed packaging films were subjected to MA packaging study with capsicum and found to be at par with low-density polyethylene + linear low-density polyethylene in maintaining the texture, colour and overall market quality.

Keywords: Biodegradable film, characterization, extrusion blown film, PBAT, polyethylene glycol, polylactic acid.

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TODAY, polymers have become a necessary part of contemporary life because of their desirable properties including durability and resistance to degradation. Worldwide production of plastics was approximately 322 million tonnes in 2015 which is a 3.5% increase compared to 2014 (ref. 1). In 2013, India produced 8.5 million tonnes of plastic[2] and about 43% of annually produced polymers are utilized by the packaging industry, which is more than the world average of 39% (ref. 3). Currently, about 99% of all polymeric materials are produced by the petrochemical industry, i.e. they are produced from fossil (non-renewable) resources[2] and manufacture of these petro plastics is energy-intensive which results in the emission of large quantities of greenhouse gases (GHGs) such as carbon dioxide that contribute to global warming. Burning of plastics generates toxic emissions such as carbon monoxide, chlorine, hydrochloric acid, dioxin, furans, amines, nitrides, styrene, benzene, 1,3-butadiene, CCl_4 and acetaldehyde which pose a threat to the environment as well as public health[4,5]. So, with the increased use of plastics, the burden on the environment is also increasing. In addition to environmental impacts caused by the mere production of polymers and plastics, there is a growing burden of waste generated when users discard products that are no longer needed. Waste has been a pressing problem for many years; in 2013, India produced 5.6 million tonnes plastic waste[4,6,7]. With increasing mass consumption of products with a short life span, the amount of waste is also going to increase rapidly. Dumping grounds have numerous potential negative environmental impacts (seepage of leachate into the groundwater, odour, destruction of the local flora and fauna, local changes in the environment, soil pollution), and they also require a lot of space. Waste plastics that in one way or another, find their way into the natural environment, represent an even greater danger[8–10]. So, the environmental impact caused by excessive quantity of non-degradable waste materials is necessitating research and efforts are on to develop new biodegradable packaging materials that can be manufactured with the utilization of environmentally friendly raw material[11,12]. The need for the replacement of petroleum-based plastic with biodegradable plastic is merely because production of conventional plastics consumes 65% more energy than producing bioplastic. Also conventional plastics are mostly toxic; these plastics last a long time and do heavy damage to environment. Therefore, these plastics are absolutely unsustainable and bioplastic is more sustainable. Moreover biopolymer saves 30–80% of greenhouse gas emissions and provides longer shelf-life than normal plastic[2,3,13,14]. Thus biopolymers in the form of packaging materials are key innovations that can help in reducing the environmental impact of plastic production and can have high value generation potential from the agriculture feed stocks[5,15–17].

Polylactic acid (PLA) is one of the most important biodegradable polyesters with many excellent properties and has been widely applied in many fields, especially for biomedical and packaging applications. PLA possesses good biocompatibility and process ability, as well as high strength and modulus[11,13,14,17–19]. Biopolymers based on their properties can be used for food packaging applications. They have the potential to replace the polymeric films used for packaging fresh produce. The application of a biodegradable film as a barrier between fruits and vegetables and their surroundings is becoming increasingly important because consumers demand hygienic and sanitary products. Modified atmosphere packaging (MAP) has been used to extend the shelf-life of fruits and vegetables, and is considered to be an effective method in preventing microbial and insect contamination[20]. Sealed packaging such as MAP is intended to suppress microbial growth, retard respiration, ripening, and senescence and inhibit oxidative reactions which require free oxygen[21–23]. Green bell peppers are usually harvested when they are of marketable size and bright green. The main post-harvest issue with capsicum is its relatively low shelf life, susceptibility to chill injuries and high amount of moisture losses in term of shrinkages. MAP of capsicum is mainly done in plastic polymeric films that are contributing to several environmental problems. Thus, the study was undertaken to develop and characterize the biodegradable films using blown film extrusion and to evaluate the developed film for MAP of capsicum.

PLA, polyethylene glycol (PEG) and polybutylene adipate terephthalate (PBAT) were used for development of biodegradable films. The films of blends were produced from developed grits via the single screw extruder blown film machine. The temperatures of barrel zones I, II, III, were set at 165°C, 165°C and 170°C and the temperatures of candle filter zone, rotating kothi zone and die were set at 170°C, 170°C and 160°C. The speed of the screw rpm and nip roller rpm was set at 115–120 and 12–15 respectively. The blow-up ratio (BUR) of the bubble was 2.5 : 1. This setting produced a bubble with an average thickness of 0.03 mm. The biodegradable films developed are shown in Figure 1.

The film properties, namely haze tensile strength, elongation strength, tear strength, oxygen transmission rates and water vapour transmission rates were measured using standard ASTM methods. The characterizations namely differentials scanning calorimetry (DSC), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and X-ray diffractions (XRD) of developed biofilms were done using given ASTM methods.

The MA packaging study of the developed films was carried out for capsicum harvested at standard maturity from the field. For this MA package of size 28 × 16 cm having packaging area for the transmission of gas of 0.0896 m^2 was considered for 0.35 kg of produce. The capsicum were MA packed (Figure 2) and stored for study at ambient (25°C) and 8°C temperatures and the variations in quality parameters and gaseous composition were monitored at regular intervals. MA packaged capsicum using low-density polyethylene (LDPE) + linear low-density polyethylene (LLDPE) (60 μ) and unpacked sample were taken as control.

Three-factor analysis of variance was conducted using Design-Expert 7.0.0®. General factorial method was used to find the two-factor and three-factor interaction effect of temperature, packaging systems and storage period on the individual quality parameters of capsicum[24]. From this analysis, predictive equations were obtained for predicting the individual quality parameter of capsicum at any combination of temperature, packaging system and storage periods. A second-order polynomial equation was considered to determine the effect of temperature, storage periods and their interaction on the quality parameters of different packaging methods and unpacked sample.

To approximate second order polynomial equation the following form was assumed

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1 x_2, \quad (1)$$

where y is the predicted response (dependent variables); b_0, b_1, b_2, b_{11}, b_{12} and b_{22} are the regression coefficients determined using the regression analysis using Origin 8.5v software; and x_1, x_2 are independent variables (factors), i.e. the temperature and storage period respectively.

To determine the extent of fit of the above second order polynomial equations with experimental data, statistical parameters namely R^2 (coefficient of determinations) and root mean square error (RMSE) were analysed.

The haze %, tensile strength, oxygen transmission rate (OTR) and water vapour transmission rate (WVTR) parameters varied from 10.65% to 28%, 48.3 to 56.49 MPa,

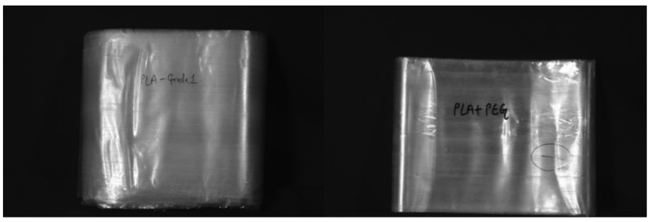

Figure 1. Developed biodegradable films.

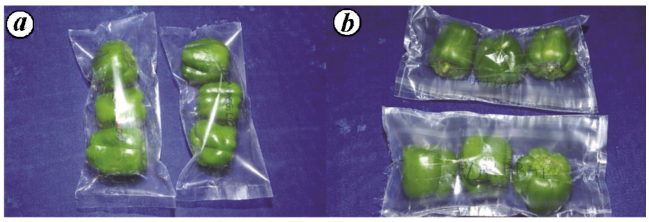

Figure 2. ***a***, PLA + PEG MA package. ***b***, PLA + PBAT (10%) MA package.

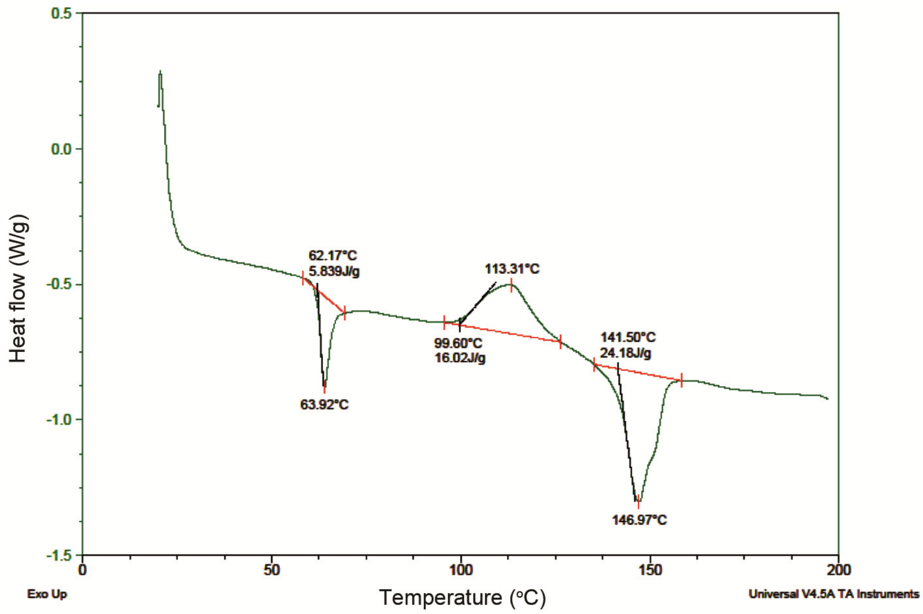

Figure 3. DSC graph showing T_g, T_m and T_c for PLA + PBAT film.

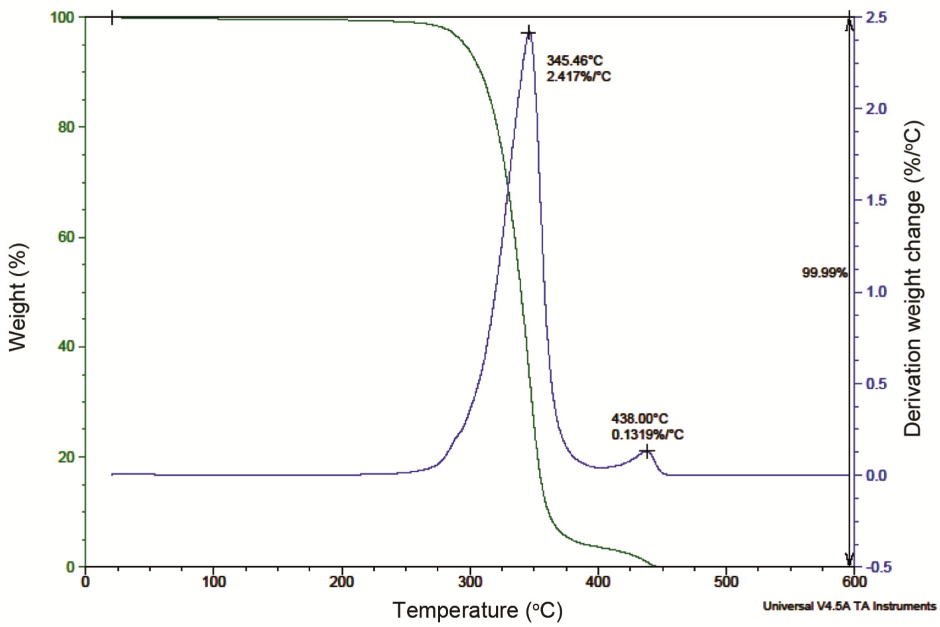

Figure 4. TGA analysis of PLA + PBAT films.

194.55 to 318.25 cc/m^2/day and 175 to 318.18 (g/m^2/day) respectively for developed films. The study shows that better haze properties in the biofilm can be achieved by compatibilizing with PEG. Oxygen transmission rates showed a declining trend in developed biodegradable films compared to the LDPE + LLDPE films which may be attributed to the formation of a tortuous path, i.e. the oxygen molecule had to pass through several hinderances while permeating inside the film because of dispersed cellulose particles inside the PLA matrix.

The water vapour transmission rate of PLA shows increased trends with the addition of PBAT; this may be due to the plastisizing effect responsible for increased free volume of PLA matrix.

Differential scanning calorimetry study indicates the material behaviour with respect to temperature. In developed films glass transition, crystalline and melting temperature varied from 63.92 to 65.74; 109.91 to 113.31; and 146.81 to 146.97 respectively. DSC results showed that there is no variation in glass transition temperature,

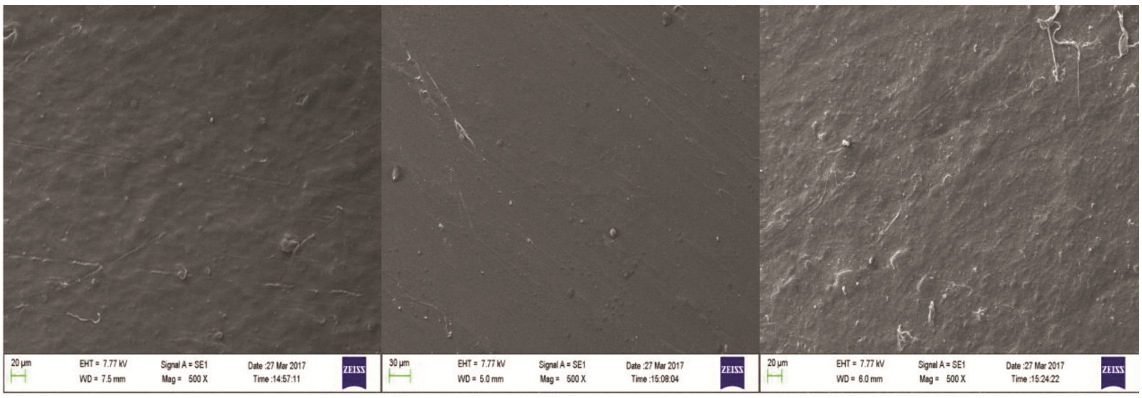

Figure 5. SEM images of PLA, PLA + PEG and PLA + PBAT.

crystallization temperature and melting temperature of these films. DSC graph for PLA + PBAT film is shown in Figure 3.

The thermogravimetric analysis indicates the percent weight loss of the films with temperature. Thermal degradation of virgin PLA takes place in a single weight loss step with degradation peak at 349.77°C compared to PLA + PBAT blended, that took two weight loss steps (Figure 4). FTIR study was used to monitor the absorption peak shifts in specific regions to determine the known functional group interactions of the PLA with various types of materials. In all the films the absorption peaks appeared at 1451.2–1451.7 and 2921.2–2944.3 cm^{-1} corresponding to asymmetrical deformation of C–H bond. The stretching of C=O band vibration appeared at 1745.2–1745.7 cm^{-1} in PLA, PLA + PEG and PLA + PBAT film. From the fracture SEM micrographs, there was smooth surface texture for films and no interfacial differences were visible indicating the presence of a single phase and structural ingregrity of the films.

SEM micrographs of virgin PLA showed smooth surface texture for films. No interfacial differences are visible indicating the presence of a single phase. SEM micrographs of PLA + 1% PEG also showed smooth surface texture for films (Figure 5). In this case too, no interfacial differences are visible, indicating the presence of a homogenous phase. Further, the surface has become smoother compared to that of PLA, indicating the plasticizing effect of PEG. SEM micrographs of PLA + 10% PBAT displayed comparatively rougher surface, proposing heterogeneity in the blend. The interface between the two components is not well-defined indicating well dispersed PBAT domains within PLA matrix. The presence of lower amount of PBAT domains would have led to this phenomenon.

The variation in physico-chemical quality attributes of capsicum under MA packaged (PLA virgin, PLA + PEG, PLA + PBAT and LDPE + LLDPE) with those of the control sample was comprehensively evaluated and compared at 8°C and 25°C storage temperatures (Figure 6). The PLW for controlled capsicum was significantly higher than the samples of MA packages stored at 25°C and 8°C temperature. The PLW in developed MA packages was found to be 1.5–1.7% wherein it was 16% at the end of 8 days at 25°C. It showed that MAP packages were effective in preventing water losses from capsicum (Figure 6). For capsicum it is recommended that a weight loss greater than 5% of the initial weight would cause reduction in the retail value. Results obtained from the study are similar to studies carried out by Ohta *et al.*[25] and Koide and Shi[26]. One of the main factors used to determine the quality and post-harvest shelf-life of commodities is the loss of firmness during storage[27]. The initial value of firmness of fresh capsicum was 56.07 ± 2.1 N. A trend of continuous decline of firmness was observed in all the MAP packages made up of different films stored at 8°C and 25°C. However the unpackaged capsicum at both the storage temperature showed a steep and significant decline of firmness. The maximum firmness of capsicum was observed in LDPE + LLDPE packaging system (42.86 N) followed by PLA (36.48 N), PLA + PEG (34.08 N) and PLA + PBAT (31.99 N) after 12 days of storage at 25°C. The same trends were observed during storage of capsicum at 8°C using developed packaging system. However, firmness decreased with increasing temperature. Thus, it appears that MA packaging with the developed biodegradable films and LDPE + LLDPE film significantly slowed down the softening of capsicum during storage. The MAP study carried out by Howard and Hernandez-brenes[28] and Manolopoulou *et al.*[29] are in agreement with the obtained results.

The colour parameters L^* and b^* in control samples at 8°C and 25°C showed significant decline whereas a^* did not change significantly during storage. In all the MAP packages stored at 25°C and 8°C the change in a^* and L^* was minimal from the initial value after 12 and 24 days respectively. The hue angle of fresh capsicum was 110.27° for the control sample; after 8 days of storage it reached 123.41° at 25°C storage temperature; in case of 8°C storage temperature it reached 122.93° after 12 days

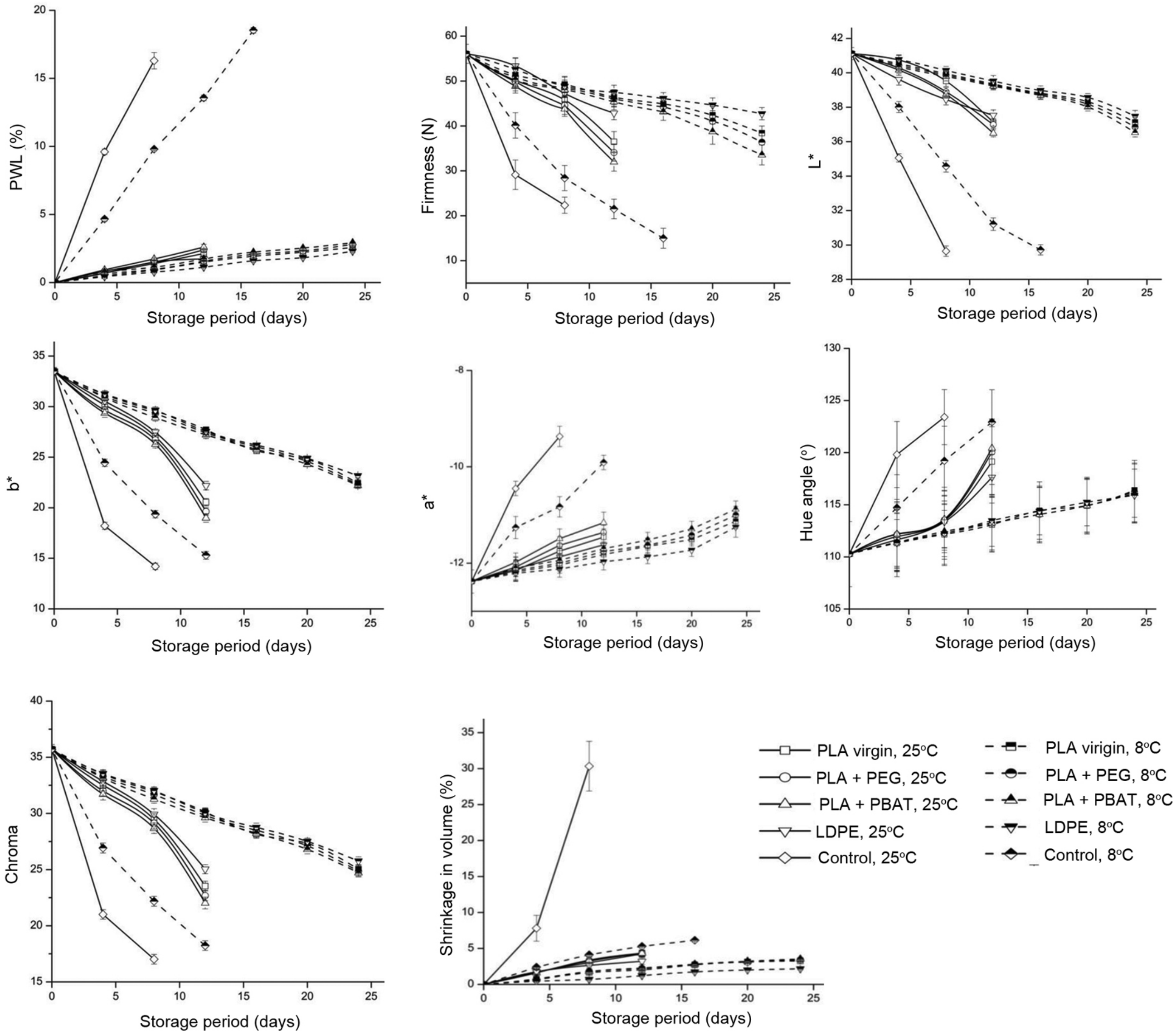

Figure 6. Variations in quality parameters of capsicum stored under various MAP systems and control at 8°C and 25°C.

of storage. The hue angle of capsicum packed under different packaging systems varied in the range 117.64–120.43°C after 12 days of storage at 25°C storage temperature. At the same time the hue angle of capsicum packed under different packaging systems stored at 8°C storage temperature for 24 days varied in the range 115.9–116.26°. Less change in hue angle was observed of capsicum packed under different packaging systems. The chroma of fresh capsicum was 35.72 and at the end of 12 days of storage it reached to 22–25 for all the packaging systems stored at 25°C. However, at the same time for capsicum stored at 8°C, it reached 24.72–25.76 after 24 days of storage. The most important parameter that should be considered during the storage of capsicum was % shrinkage in volume. Maximum % shrinkage volume was observed in capsicum stored under control condition at 25°C (30.34%) after 8 days of storage, followed by capsicum stored under control conditions at 8°C (6.14%) after 16 days of storage. The capsicum stored under different packaging conditions at 25°C varied from 3.47% to 5.30% after 12 days of storage and at the same time, capsicum stored at 8°C under different packaging system varied from 2.5 to 3.96 after 24 days of storage period.

Three-factor analysis of variance (ANOVA) revealed that direct effect, as well as two and three factor interaction effects of temperature, packaging system and storage periods were found to have significant effect on quality parameters of capsicum at 1% level of significance except for two factor interaction (temperature and packaging system) on titratable acidity. The estimate of parameters obtained from three factor ANOVA along with their standard error for individual quality parameters was determined and the predicted equations in coded form were developed. From these equations the individual quality parameters of capsicum can be obtained at any temperature, storage period and packaging system or any interaction of these.

The physical and morphological characterizations of the developed commercial biodegradable films were found suitable for the food packaging applications. Modified atmosphere packaging in developed biodegradable films maintained the quality of capsicum up to 12 days and 24 days at 25°C and 8°C respectively compared to unpackaged capsicum having shelf life of 4 days and 9 days at 25°C and 8°C respectively. The developed packaging films were found to be effective in maintaining the overall market quality of capsicum. The results suggest that the developed biodegradable film provide an alternative to the petroleum-based polymeric film for MA packaging of fruits and vegetables.

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