Blending of Low-Density Polyethylene with Vanillin for Improved Barrier and aroma-releasing Properties in Food Packaging

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ABSTRACT: Modification of low-density polyethylene (LDPE) with vanillin to obtain flavored packaging film with improved gas barrier and flavor-releasing properties has been studied. The modification of LDPE with vanillin was monitored by Fourier transform infrared spectroscopy, wherein the appearance of new peaks at 1704.7, 1673.6, and 1597.2 cm^{-1} indicates the incorporation of vanillin into LDPE matrix. Films of uniform thickness were obtained by the extrusion of modified LDPE. Modified LDPE was found to have significantly higher gas barrier properties and grease resistance. Sensory quality of food products viz, *doodhpeda* (milk-based solid soft sweet), biscuit, and skimmed milk powder packed in LDPE-vanillin film showed that the *doodhpeda* sample had clearly perceptible vanilla aroma, whereas biscuit had marginal aroma and skimmed milk powder did not have noticeable aroma. When viewed in the light of imparting desirable vanilla aroma, results of the study indicated that LDPE-vanillin film has better prospects as a packaging material for solid sweets with considerable fat content when stored under ambient conditions. The release of vanilla aroma was further confirmed by gas chromatography–mass spectrometery analysis. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3732–3741, 2009

Key words: polyethylene; modification; barrier properties; FTIR; odor profile

INTRODUCTION

Plastics have gained a unique position in packaging technology for a number of reasons including, high tensile strength and elongation at break; good barrier properties against moisture; lower cost; higher energy effectiveness; light weight; and good water resistance.[1] In food packaging, polyethylene, especially low-density polyethylene (LDPE), is the most widely used polymer. However, the use of pure LDPE is restricted because of some of its inherent properties such as, a high oxygen and carbon dioxide transmission rate (OTR and CO_2TR), poor grease resistance, and limited adhesion to other substances. Hence, it is mostly used as laminated films in combination with other films that possess superior barrier properties, which invariably require the use of adhesives or as co-extrusion for better packaging applications.[2] The intrinsic properties of polyethylene mainly arise from its totally nonpolar nature. The structural modification of LDPE may be helpful in improving some of its properties and thereby, enhancing its utility by decreasing the need for its lamination with expensive materials such as polyester and nylon. The structure–property relationship is a powerful tool for designing polymers for special applications. Chemical modification or blending with readily available polymers offers an attractive route to improve the polymer's inherent characteristics or the creation of new ones. There are a few reports on the modification of polyethylene with carbonyl functional unsaturated compounds to improve adhesion.[3–6] Modification of polyethylene with maleic anhydride and *n*-phenylmaleimide results in anticorrosive coatings.[7,8] There have been attempts to modify the surface of LDPE films also by treatment with chromic acid,[9] SO_3,[10] and by low-pressure oxygen plasma treatment[11] to improve adhesion properties. But there is very little information available on modification of LDPE aimed at the improvement of barrier and flavor-releasing properties. The treatment of LDPE with oleum and SO_3[10] and diisocyanates[12] has been carried out to decrease the OTR. Most of the studies on LDPE resins, however, have been concerned with the improvement of its impact strength,[13–15] tear strength,[16,17] and also blending with starch for biodegradability, food packaging,[18–21] mechanical, and thermal studies.[22–26]

The consumer considers flavor as one of the most important attributes for the acceptance of food. Packaging materials that come in close contact with the foods can influence its flavor. In odor profiling by a sensory panel helps in assessing the effect of

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packaging material on the flavor quality of the food packed in it. Odor profile of palm oil samples stored in different structured film packages has been reported.[27] A US patent discusses flavored film that quickly and completely disintegrates when it comes in contact with human mucosal tissue in the oral cavity. It is stated that this may be used in food items to impart flavor and optionally to impart functional qualities to the food.[28] Another US patent states the use of rapidly disintegrating flavored film for precooked foods.[29] This work was taken up with an objective of incorporation of vanillin into the polymer (LDPE) matrix and studying its effect on gas barrier properties, grease resistance; sensory quality of the film, and the foods packed in it.

EXPERIMENTAL

Materials

All solvents used in the experiment were purified by distillation before use. LDPE (24FS040, Reliance Industries Limited, Mumbai, India) was purified by dissolving it in CCl_4 and re-precipitating it with acetone, followed by soxhlet extraction for 16 h with acetone. Vanillin (Sisco Chemicals, Mumbai, India) was used without further purification. *Doodhpeda* (milk-based solid soft sweet prepared by condensing milk with sugar), biscuit, and skimmed milk powder were purchased from local market and were used as such for storage and sensory analysis.

METHODS

Blending of LDPE with vanillin

LDPE was dissolved in CCl_4 (10% w/v solution) by refluxing in a two-necked, 1-L, round-bottom flask fitted with a condenser on a mechanical stirrer. After complete dissolution, 1% vanillin (based on LDPE weight) was dispersed with constant stirring for 2 h to have uniform mixing. Addition of vanillin was optimized upto 1%, because the limit of vanillin[30] added in most food product is less than 1%. The LDPE solution with dispersed vanillin was dried as physically blended fine powder by constant stirring. The homogenously blended LDPE–vanillin powder was used for extruding films. Plain LDPE powder was also prepared as per the above procedure without adding vanillin.

Extrusion process for plain LDPE and LDPE–vanillin

Plain LDPE and LDPE–vanillin films were extruded using Thermo Haake single-screw extruder (Rheomix 252 p, Die; 10 mm width and 0.5 mm slit height, screw dimension 3 : 1, 25 d) Temperatures of various zones like feed zone, compression zone, metering zone, and die zone of the extruder were set at 110, 120, 130, and 140°C, respectively. The screw rotation was set at 60 rpm. Once the set temperatures of various zones were attained, plain LDPE and LDPE–vanillin samples were fed separately through the feed hopper into the feed section of the barrel and films were made.

FTIR spectral studies

Thin films of uniform thickness (75 μm) were used for obtaining the IR spectra of using FTIR-RAMAN Nicolet 5700. All measurements were carried out at 20°C in anhydrous conditions with air as the background. For each sample, 32 scans at a 2-cm^{-1} resolution were collected in the range of 4000–400 cm^{-1}. The spectra were then analyzed with a curve-resolving technique based on a linear least squares analysis to fit a combination of Lortzuein and Gaussian curve shapes.[2,12]

Physicomechanical studies

Density was determined by floatation method at 25°C using CCl_4 and *n*-heptane as solvents. The film (1.5 × 1.5 cm^2) was immersed in 5 mL heptane in a small beaker. CCl_4 was taken in a burette and added drop wise to the beaker until the film floated in the middle of the solution. The density of the film was calculated as follows.[31]

$$\text{Density} = \frac{V_1 d_1 + V_2 d_2}{V_1 + V_2} \quad \text{g/mL}$$

where V_1 is the volume of heptane (mL), V_2 is the volume of CCl_4 (mL), d_1 is density of heptane (g/mL), and d_2 is density of CCl_4 (g/mL).

Tensile strength and percentage elongation at break for the plain LDPE and LDPE–vanillin films were measured as per ASTM D-882 method using LLOYDS universal testing (LLOYDS-50K, London, UK) instrument at an ambient temperature of 25 ± 2°C and average of five measurements is reported.

Heat seal strength is the measure of the force required to pull apart the pieces of film that have been sealed together. The test was carried out for plain LDPE and LDPE–vanillin films as per ASTM D 1876 using LLOYDS universal testing instrument. Two strips of same plastic films (6.25 × 2.5 cm^2) were sealed together using an HP impulse sealer (Sunray industries, Mysore, India) at 8.4 Kgf/cm^2 pressure for 16 s to get a standard seal width of 10 mm. Free ends of the sample were mounted on two grips of the tensile testing machine and the movable jaw driven at a constant rate of 200 mm/min, breaking the sealed area apart. The load required to break the

seal of the sample was noted. Seal strength was calculated by dividing the load at break by the seal width. The average of five measurements is reported.

Internal tearing test (in Newton) of plain LDPE and LDPE–vanillin films was determined as per TAPPI standard test method (ASTM, 1988) using LLOYDS universal testing instrument. This involves the determination of force necessary to propagate a tear in the specimen. The specimen was cut into a size of 120 mm length and 25 mm width. The aforementioned specimen was cut longitudinally up to 70 mm in the middle. One edge of the cut specimen was fixed to upper jaw and the other to lower jaw of the tensile instrument. The movable jaw was driven at a constant rate of 200 mm/min, tearing the film apart. The load required to tear the sample was noted. Internal tearing resistance strength was calculated by dividing the maximum load for tearing film by cross-sectional area.

Barrier properties

Water vapor transmission rate (WVTR)[32] was gravimetrically measured as per ASTM E 96–95, and the results were expressed as grams of moisture vapor permeated through the film per square meter per day at a 90% relative humidity (RH) gradient at 38°C; the OTR and CO_2TR of films were measured as per ASTM D 1434-66, and the results were expressed as milliliters per square meter per day at atmospheric pressure.

Grease resistance[33] of films was measured using pouch method. Pouches of 6 × 10 cm^2 in size were made and filled with 50 mL groundnut oil colored with 1% Sudan red dye, sealed, and placed over a white sheet of paper at 40°C in an oven. The pouches were periodically checked for any oil seepage as indicated by appearance of red spot on the paper. Grease resistance is expressed in number of days taken for the appearance of red spot due to seepage of oil.

Optical properties

Optical properties were measured by a Suga test using Digital Haze meter (model HGM-2DP, Japan). The haze behavior of dust and grease-free films was recorded as per ASTM D-1003-61 method.

Thermal studies

Differential scanning calorimetry

Studies on various melting and crystallization parameters of plain LDPE and LDPE–vanillin films were determined by differential scanning calorimeter (DSC) (model DSC 2010, Dupont) with a thermal analyst 2100 system (TA instruments, US). Temperature and heat flow calibration of the equipment was done with indium under conditions similar to those used in the experiments with the samples. All the experiments were carried out with sealed empty pan as the reference, with N_2 gas flushing. Sealed pans with samples (5–10 mg) were first cooled to −50°C, held isothermally for 1 min, and then ramped (10°C/min) to 200°C to obtain the heat flow curves. Temperature on set, glass transition temperature (T_g), crystalline melt temperature(T_p), temperature of completion of the endotherm during melting, exotherm during crystallization, and heat of enthalpy (ΔH) were obtained on thermograms using TA universal thermal analyzer software.

Thermogravimetric analysis

A thermal weight change analysis instrument (thermogravimetric analysis [TGA], Q50, TA Instruments, Delaware) was used to measure the amount and rate of change in weight of the material as a function of increasing temperature or time, in a controlled atmosphere. The samples (8–10 mg) were kept in a platinum crucible and heated in the furnace, from 30 to 700°C, at the rate of 20°C/min, under nitrogen stream being flushed at the rate of 40 mL/min. The percentage weight loss was plotted against temperature.

Food compatibility

Films were evaluated for their suitability for food contact application by estimating overall migration of additives into different food simulants as per IS: 9845-1998 specifications. Films were exposed to food simulants like distilled water, 3% acetic acid, 50% ethanol (representing aqueous foods, acidic foods, and alcoholic beverages, respectively) at 40°C for 10 days simulating the filling and storing condition at room temperature and *n*-heptane (as fat simulant) at 38°C for 30 min as per IS: 9845-1988. Overall migration of additives was determined by exposing the film sample to food simulant under stipulated conditions of time and temperature. Extracted simulant was evaporated and migrated material was estimated gravimetrically. The results were expressed as milligram per square decimeter.

Sensory analysis—methodology

For food products

Pouches of required size were made of LDPE and LDPE–vanillin films for packaging of selected food samples namely, high fat (*Doodhpeda*), medium fat (biscuit), and low fat content (skimmed milk powder). The packed products were stored under

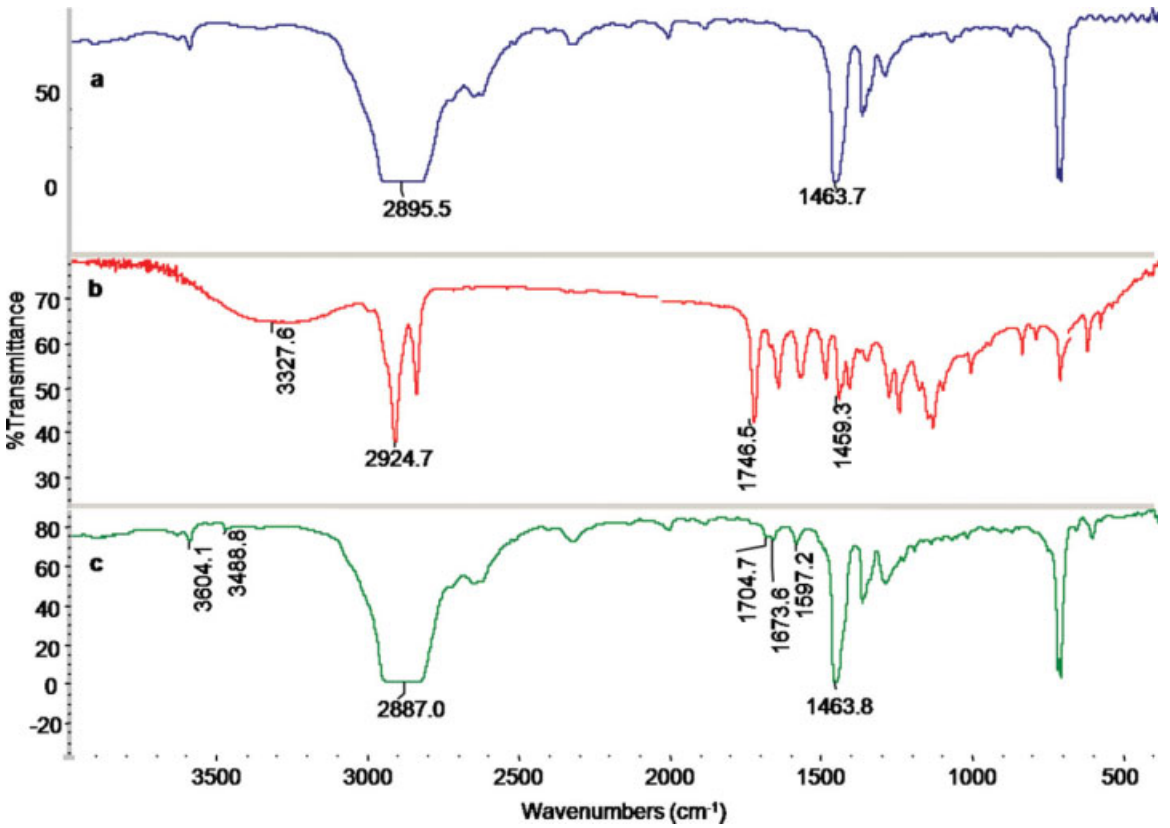

Figure 1 FT-IR characteristics of (a) LDPE, (b) vanillin, and (c) LDPE–vanillin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

simulated ambient (27°C; 65% RH) and accelerated (37°C; 90% RH) conditions.

Withdrawal schedule

Initially, all the food samples were sensorily evaluated before storage. Stored samples of *doodhpeda* were withdrawn at the end of 7 days, biscuits at the end of 30 days, and skimmed powder at the end of 30 and 60 days and subjected to sensory analysis. Sensory analysis of the samples was carried out in separate sessions in "sensory booth" under white fluorescent light, with the booth area maintained at temperature of 20 ± 2°C and RH 50 ± 5%. Descriptors for the quality of samples (food and films) were generated, focusing on the aroma imparted by the packaging material. A suitable score card was developed using these descriptors.

Doodhpeda and biscuit were served in porcelain containers coded with three-digit random numbers, to panelists. Skimmed milk samples were tested in two stages: (a) in powder form by odor profiling (5 g in 25 mL stoppered conical flasks that were coded) and (b) as milk reconstituted with hot water (60°C) in the ratio 1: 6. This was served in glass containers coded with three-digit random numbers. Plain water and puffed rice were served as palate cleansers, along with the samples.

Sensory analysis of the samples was carried out by a trained panel of 10 judges. A structured line scale of 0–10 cm was used, anchored at the beginning and end as "None" and "High", respectively. Panelists were asked to mark the perceived intensity of attributes by drawing a vertical line on the scale and writing the code of the sample. The scores for each attribute of a given sample were tabulated and mean values are reported.

Sensory odor profiling of film

Odor profiling of the film was carried out as per the IS 8639 method. Films, LDPE, and LDPE–vanillin, each measuring 1000 cm^2 in area, were cut into small pieces (2 cm^2) with minimum handling. These were transferred to 250 mL conical flasks separately, stoppered, and coded with three-digit random numbers. For each of the two films, eight such samples were prepared—four in dry condition and four in wet condition simulated by adding 10 mL of water. The conical flasks were stored under ambient and accelerated conditions. After 24 and 48 h, samples were withdrawn and subjected to odor profiling by a trained sensory panel. Panelists were asked to take

TABLE I
Physicomechanical and Barrier Properties of LDPE–vanillin Films

	Physicomechanical properties						Barrier properties[d]			
								GTR[c]		
Material films	Density g/cc		Tensile strength[a] (MPa)	% Elongation[a]	Heat seal strength[a] (MPa)	Tear strength[a] (MPa)	WVTR[b]	O_2	CO_2	Grease resistance (Day)
Plain LDPE	0.9296	MD	4.0 ± 0.072	72.8 ± 1.456	3.1 ± 0.065	0.92 ± 0.018	15.6 ± 0.187	7566.13 ± 37.83	30987.55 ± 216.9	09 ± 0.27
		CD	3.0 ± 0.06	54.63 ± 1.256	2.3 ± 0.052	0.82 ± 0.015				
LDPE–vanillin	0.9367	MD	4.4 ± 0.083	79.4 ± 1.667	3.4 ± 0.078	1.01 ± 0.021	16.9 ± 0.219	5815.00 ± 40.70	24606.43 ± 221.45	19 ± 0.38
		CD	3.5 ± 0.07	63.14 ± 1.452	2.7 ± 0.064	0.92 ± 0.017				

Films of 25 μm with uniform thickness were used.
MD, Machine direction; CD, cross-direction.
[a] Mean ± SE; $n = 5$.
[b] g/m^2/days at 90%RH gradient and 38°C.
[c] cc/m^2/days at standard temperature and pressure.
[d] Mean ± SE; $n = 4$.

a quick sniff of the headspace volatiles by briefly opening the stopper, sniffing, and quickly closing it. The panelists were asked to indicate their response showing the intensity of perception of odor notes on the scale indicated in the scorecard.

Solid-phase microextraction/gas chromatograph/mass spectrometer

Sample preparation

Shimadzu gas chromatograph (17-A)-mass spectrometer (QP-5000) was used for odor profile of films. Pure vanillin in crystalline form was dissolved in ethanol with a working concentration of 200 ng/μL, which served as the standard for gas chromatograph (GC)/mass spectrometer (MS) analysis. The surface area of 1000 cm^2 of each film was cut into small pieces of 2 cm^2, transferred to 250 mL conical flasks, and sealed with paraffin film. Flasks were kept for 24 h for volatiles to accumulate in the headspace. Solid-phase microextraction (SPME) was performed using an SPME device (Supelco, Bellefonte, PA). The extraction was carried out using a polydimethylsiloxane (100-μm thick) fiber. The needle of SPME device was inserted into the headspace above the sample and held for 90 min to facilitate adsorption of aroma. Then, the adsorbed volatiles in the fiber were injected into the injection port of GC-MS. The fiber remained in the injector for 2 min for thermal desorption of the analytes onto the GC column.[34]

Analysis was carried out under the following conditions: column, SPB-1; column initial temperature, 50°C; column final temperature, 220°C; injection temperature, 220°C; detector, MS; detected temperature, 220°C; carrier gas, nitrogen at the flow rate of 1 mL/min; hold time, 5 min.

RESULTS AND DISCUSSION

Chemical characterization by FTIR spectroscopy

IR spectra of LDPE, vanillin, and LDPE–vanillin are depicted in Figure 1. The IR spectra of vanillin [Fig 1(b)] shows a strong band at 3327, 2924, and 1746.5 cm^{-1} corresponding to phenolic (—O—H) stretching, asymmetric stretching of alkenes (—CH—), and stretching of aldehyde (—C=O), respectively. In addition to this, peaks at 1666 and 1595 cm^{-1} corresponding to aromatic (—C=C—) stretching were also observed. The IR spectra of LDPE–vanillin in Figure 1(c) showed the presence of peaks at 1673.6, 1597.2, and 1704 cm^{-1} corresponding to (—C=C—) aromatic stretching and (—C=O) aldehyde of vanillin along with peaks at 2895 cm^{-1} (—C—H— stretching) and 1463 cm^{-1} (—C—H— bending) found in plain LDPE in Figure 1(a). This clearly indicates the incorporation of vanillin with the LDPE matrix.

TABLE II
Optical Properties of LDPE–vanillin Films

Material films	Total transmittance[a] (T_t %)	Total diffuse[a] (T_d)	Percent parallel	Haze [a]
Plain LDPE	92.6 ± 0.741	12.5 ± 0.125	80.1	13.5 ± 0.168
LDPE–vanillin	91.7 ± 0.825	25.4 ± 0.305	66.3	28.0 ± 0.364

Films of 25 μm with uniform thickness were used.
[a] Mean ± SE; $n = 3$.

Physicomechanical properties

Physicomechanical properties of LDPE–vanillin film were compared with those of the plain LDPE film in Table I. It was observed that in LDPE–vanillin film there was an increase in tensile strength up to 16%, percentage elongation at break was higher by 15%, heat seal strength and tear strength were increased by 17% and 12%, respectively. This increase in the mechanical properties was due to the incorporation of vanillin in the LDPE matrix by uniform and homogeneous blending, which may act as a filler and induce reinforcing effect. These findings are in accordance with similar reports.[35,36]

Barrier properties

Values of WVTR, OTR, CO_2TR, and grease resistance are given in Table I. The WVTR values showed a marginal increase of 8% in LDPE–vanillin film compared with plain LDPE film, indicating that the polarity change in the LDPE–vanillin did not affect the properties of LDPE adversely. However, blending of vanillin into LDPE matrix significantly decreased the OTR and CO_2TR and increased the grease resistance. Oxygen barrier property was improved by 24% and that of carbon dioxide was improved by 20% in the LDPE–vanillin film. The grease resistance for LDPE–vanillin was 19 days compared with 9 days for the LDPE films at 40°C, showing a significant improvement of 137%. Usually, polymeric materials such as polyethylene, because of their nonpolar nature, are good barriers of water vapor transmission but poor barriers of gases. Materials such as polyester, nylon, and polyvinyl chloride, because of their polar nature, are good barriers of oxygen but poor barriers of water vapor. The polarity difference caused by the incorporation of vanillin (polar compound) into LDPE matrix seemed to be enough to cause an appreciable reduction in OTR and CO_2TR and an increase in grease resistance properties.[2,12,35]

Optical properties

Percentage transmittance, total diffuse, percent parallel, and haze for LDPE and LDPE -vanillin films are shown in Table II. There was a very little decrease in percentage transmittance from 92.6 in LDPE to 91.7 in LDPE–vanillin films. Haze values increased from 13.5 in LDPE to 28 in LDPE–vanillin films. The increase in haze after incorporation of vanillin into the LDPE matrix could be due to the scattering or diffusion of light radiation by vanillin.[21,36,37]

DSC studies

Typical DSC thermograms for the heating and cooling curves of the plain LDPE and LDPE–vanillin are shown in Figures 2 and 3. T_g, the glass transition, T_p, the area under the DSC curve (ΔH), and the melt

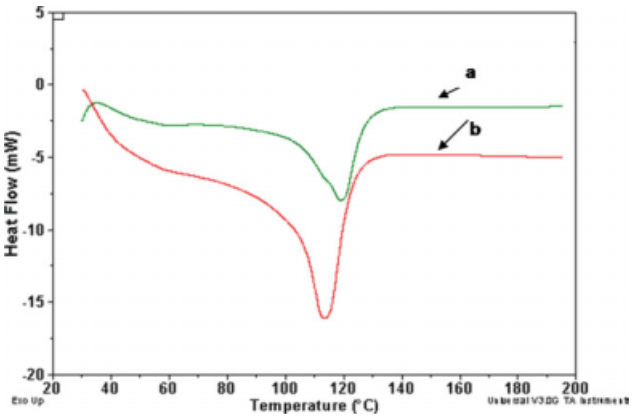

Figure 2 DSC heat flow curves for (a) LDPE and (b) LDPE–vanillin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

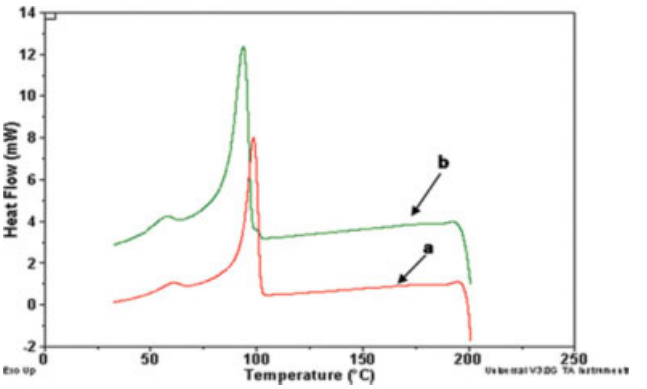

Figure 3 DSC cooling curves for (a) LDPE and (b) LDPE–vanillin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
DSC Melt Characteristics Parameters of LDPE–vanillin Films

	Heating curve				Cooling curve		
Material films	T_g (°C)	T_p (°C)	Melt range	ΔH (J/g)	T_p (°C)	Crystalline range	ΔH (J/g)
LDPE	46.23	118.92	65	66.51	98.49	36	77.43
LDPE–vanillin	55.17	113.83	62	69.73	93.62	32	60.30

range values are given in Table IV. T_g increased from 46.23 for plain LDPE to 55.17 in LDPE–vanillin film correspondigly, T_p decreased from 118.92 to 113.83°C, which may be due to the incorporation of vanillin into the LDPE matrix. Similarly, there was a marginal reduction in the melt range area under the melt curves from 65 in plain LDPE to 62 in the LDPE–vanillin. As shown in Table III, in crystallization melt, T_p decreased from 98.49° C for plain LDPE to 93.62°C in LDPE–vanillin film. However, there was a marginal decrease in crystallization range from 36 for plain LDPE to 32 in LDPE–vanillin, but a reduction in the enthalpy of crystallization for LDPE–vanillin was observed. This may be due to the decrease in crystalline nature in the LDPE–vanillin system. The enthalpy value of 69.73 for LDPE–vanillin compared with 66.51 for plain LDPE during melting is probably due to the higher heat sensitivity of vanillin present in LDPE–vanillin film.

Thermogravimetric analysis

TGA thermograms of LDPE and LDPE–vanillin are shown in Figure 4. It was observed that the thermograms shows complete degradation (100% weight loss) for LDPE and LDPE–vanillin films at 520° C. As shown in Table IV, the decomposition of LDPE and LDPE–vanillin started at 425 and 400° C, respectively. The degradation behavior of LDPE–vanillin was comparable with plain LDPE with slight changes in T_{max} from 488.56° C in LDPE to 484.24° C in LDPE–vanillin.

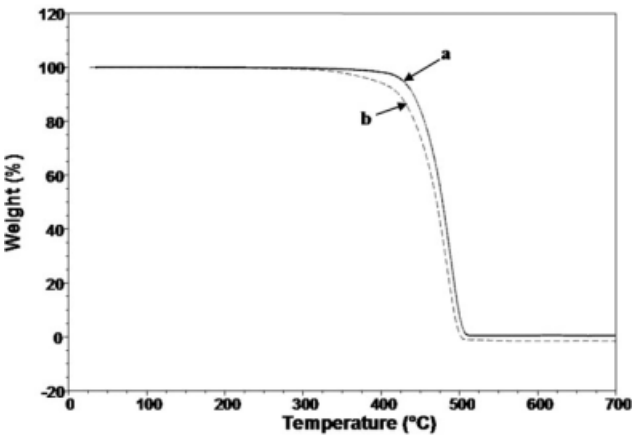

Figure 4 TGA of (a) LDPE and (b) LDPE–vanillin.

Food compatibility

Any packaging material used for food contact applications shall not transfer any additives into the food in unacceptable quantities and hence ought to be evaluated for its migration characteristics into food simulants. Migration values for LDPE and LDPE–vanillin ranged from a minimum of 0.567 in 50% ethyl alcohol to 1.6 mg/dm^2 in 3% acetic acid as shown in Table V, remained well within the limits of 10 mg/dm^2, ascertaining its compatibility for food packaging applications.

Sensory analysis

Doodhpeda

Samples of *doodhpeda* were withdrawn at the end of 7 days. Fresh sample was found to have more intense fresh and creamy aroma notes while the stored samples were less intense in these notes. As shown in Table VI, under ambient storage condition, *doodhpeda* sample packed in LDPE–vanillin was found to have clearly perceptible vanilla aroma as shown by a score of 5.0. On the other hand, sensory score for vanilla aroma was very low (0.5) for the corresponding sample stored under accelerated condition. "Fruity," an associate note of vanilla aroma, was also perceived in the sample stored under ambient condition to a greater extent (4.5). Similar pattern was observed in odor perception. This indicates that it could be advantageous to use LDPE–vanillin for packing milk-based sweets where vanilla aroma is compatible or desirable.

Biscuit

Sensory quality of stored biscuits withdrawn and evaluated at the end of 30 days indicated the pattern of vanilla aroma notes perceived in the sample packed in LDPE–vanillin and stored under ambient

TABLE IV
Thermogravimetric Analysis of LDPE–vanillin Films

	Transition temperature			
Material films	T_0 (° C)	T_{max} (° C)	T_C (° C)	% Weight loss
Plain LDPE	425.00	488.56	517.00	100
LDPE–vanillin	400.00	484.24	519.00	100

TABLE V
Food Compatibility of LDPE–vanillin Films

Material films	Over all migration[a] as per IS: 9845–1988			
	Distilled water 10 days at 40° C (mg/dm^2)	3% Acetic acid 10 days at 40° C (mg/dm^2)	50% Ethyl alcohol 10 days at 40° C (mg/dm^2)	*n*-Heptane 30 min at 38° C (mg/dm^2)
Plain LDPE	1.0 ± 0.010	1.1 ± 0.012	0.567 ± 0.003	1.189 ± 0.013
LDPE–vanillin	1.47 ± 0.017	1.6 ± 0.019	0.733 ± 0.005	1.457 ± 0.017

[a] Mean ± SE; $n = 3$; Limits < 10 mg/dm^2.

conditions shown in Table VI. Compared with control, there was significant perception ($P \leq 0.05$) of vanilla and fruity notes with a score of 3.0 and 2.0, respectively. However, the perceived levels were lower compared with those in doodh peda. It may be noted here that the fat content of biscuit is lower than that of peda. This suggests that the possible role of fat in food samples in absorption, retention, and release of aroma compounds. Vanilla aroma note in other samples was marginal.

Skimmed milk powder

Studies carried out on skimmed milk powder packaged in LDPE–vanillin film stored under ambient and accelerated conditions revealed that vanilla odor note was not perceived in milk powder. Milk reconstituted from stored milk powder, did not have perceptible vanilla aroma either.

Odor profile of films

Results of odor profiling of LDPE–vanillin film are shown in Table VII. Significant levels ($P \leq 0.05$) of vanilla, fruity, and sweetish notes were perceived in samples of LDPE–vanillin compared with their respective controls. The intensity of perception was higher (8.6) in the samples stored for 24 h than in those stored for 48 h (7.0). Panelists indicated perception of these notes to a greater extent (8.6) in samples stored under ambient conditions than those stored under accelerated conditions (4.3). Another interesting observation was that under wet conditions, except mild fruity notes, vanilla odor could not be perceived in LDPE–vanillin samples.Under ambient and dry conditions "plasticky" and "chemical" notes were predominant in LDPE samples, perceived at higher levels compared with LDPE–vanillin. Under accelerated conditions, these notes were observed at greater concentrations in LDPE–vanillin compared with LDPE. Unpleasant fatty odor was found in all the samples only under wet conditions with increasing intensity as storage period increased. They were highest in samples stored for 48 h under accelerated conditions.

SPME/GC/MS

Total ion chromatogram (TIC) along with mass spectrum (MS) of vanillin as a standard and released head space vanillin from LDPE–vanillin film samples are presented in Figure 5. GC chromatograph showed the same retention time of 14.98 min for released headspace vanillin and pure vanillin under identical GC conditions confirming the presence of vanillin released from LDPE–vanillin film. Results of MS in the form of chromatogram showed the presence of vanillin released from LDPE–vanillin film to be pure. The peaks at m/z 151 and 152 corresponding to M and M^+ along with daughter ions 1,2-dihydroxy benzaldehyde,2-hydroxy benzaldehyde,1,2-dihydroxybenzene, phenol, benzene, and cyclopentadiene at 137, 123, 109, 93, 81, and 65 established its identity as vanillin released from head space sampling of LDPE–vanillin film. Thus, instrumental data corroborated sensory data on odor profiling of the LDPE–vanillin films.[38,39]

TABLE VI
Sensory Profile of *Doodpeda* and Biscuit

Attribute	Fresh	Packed in LDPE		Packed in LDPE-Vanillin	
		Amb.	Acc.	Amb.	Acc.
Sensory Profile of *Doodhpeda*					
Odor					
Vanilla	0^{a}*	0^{a}	0^{a}	5.5^{c}	1.0^{b}
Fruity	0^{a}	0^{a}	0^{a}	3.0^{b}	0.5^{a}
Creamy	8.5^{c}	7.5^{b}	5.5^{a}	8.0^{b}	5.0^{a}
Aroma					
Vanilla	0^{a}	0^{a}	0^{a}	5.0	0.5^{a}
Fruity	0^{a}	0^{a}	0^{a}	4.5	0.5^{a}
Creamy	8.0^{b}	7.0^{b}	5.0^{a}	5.0^{a}	4.5^{a}
Sensory Profile of Biscuit					
Baked Cereal	8.5^{ba}	3.5^{a}	3.0^{a}	4.0^{a}	3.0^{a}
Vanilla	1.0^{a}	0.0^{a}	0.0^{a}	3.0^{b}	0.5^{a}
Fruity	0.5^{a}	0.0^{a}	0.0^{a}	2.0^{b}	0.5^{a}

Amb., Ambient condition; Acc., Accelerated condition.
* Different alphabets in a row indicate significant difference ($P \leq 0.05$) between the values.

TABLE VII
Odor Profile of Flavored Film

		LDPE				LDPE- Vanillin			
		Amb.		Acc.		Amb.		Acc.	
Attribute		24 h	48 h	24 h	48 h	24 h	48 h	24 h	48 h
Plasticky	Dry	5.5^{c*}	8.0^{d}	2.3^{a}	3.0^{a}	2.1^{a}	2.9^{a}	3.8^{b}	5.0^{c}
	Wet	—	—	—	—	—	—	—	—
Chemical	Dry	4.7^{c}	6.5^{d}	—	—	1.7^{a}	2.2^{a}	3.1^{b}	4.5^{c}
	Wet	—	—	—	—	—	—	—	—
Unpleasant fatty	Dry	—	—	—	—	—	—	—	—
	Wet	3.3^{a}	4.0^{a}	4.2^{a}	5.5^{b}	4.8^{ab}	7.0^{c}	5.0^{b}	7.3^{c}
Fruity	Dry	—	—	—	—	7.7^{d}	6.3^{c}	4.1	3.0^{a}
	Wet	—	—	—	—	1.2^{a}	1.9^{a}	—	—
Sweetish	Dry	—	—	—	—	6.1^{c}	5.0^{b}	4.0^{a}	3.2^{a}
	Wet	—	—	—	—	—	—	—	—
Vanilla	Dry	—	—	—	—	8.6^{c}	7.0^{b}	4.3^{a}	3.9^{a}
	Wet	—	—	—	—	—	—	—	—

Amb., Ambient condition; Acc., Accelerated condition.

* Different alphabets in a row indicate significant difference ($P \leq 0.05$) between the values.

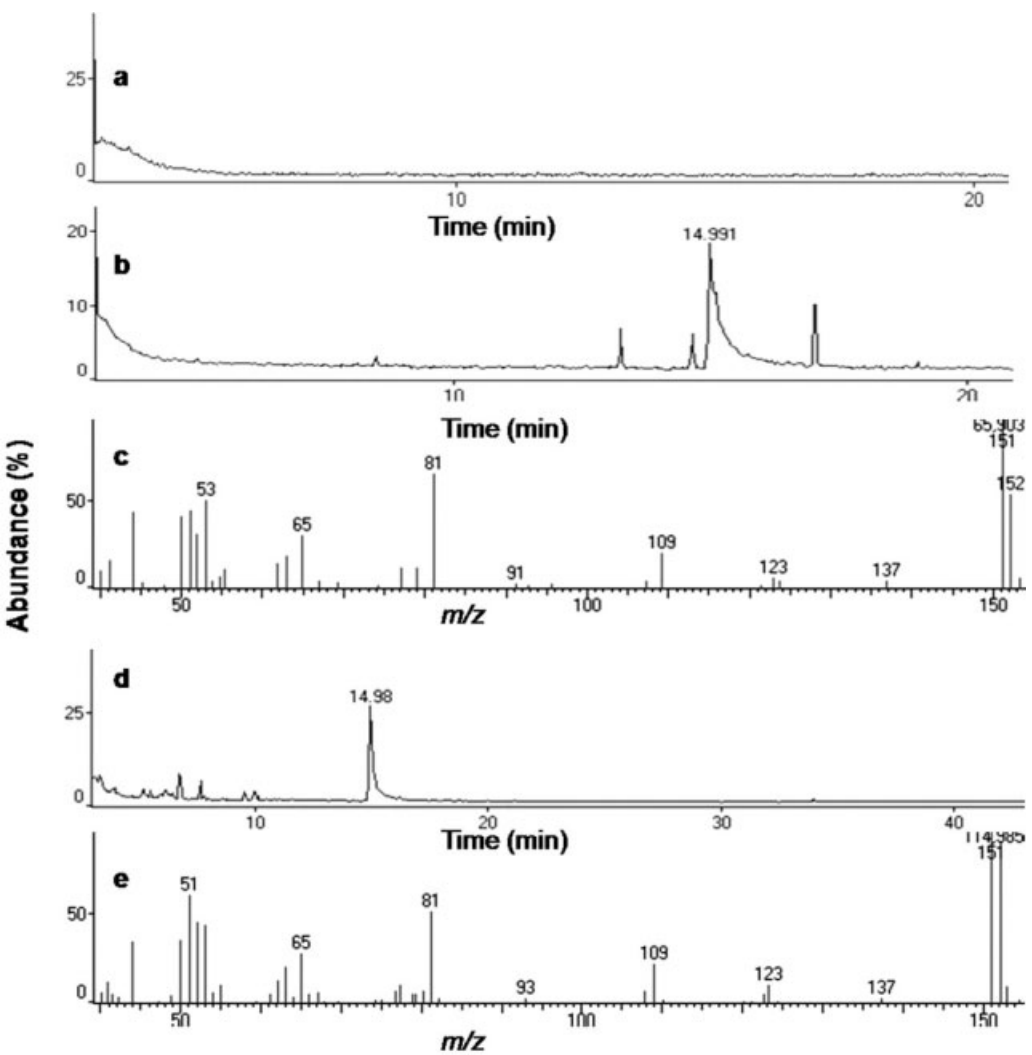

Figure 5 (a) SPME-TIC of LDPE, (b) SPME-TIC of vanillin standard, (c) MS of vanillin standard, (d) SPME-TIC of LDPE–vanillin blend, (e) MS of vanillin in LDPE–vanillin blend.

CONCLUSIONS

Blending vanillin with LDPE even at a low level was sufficient in improving oxygen and carbon dioxide barrier properties by 24 and 20%, respectively. An appreciable improvement (137%) in grease resistance was also observed. Blending did not significantly affect the other required characteristics of LDPE. There was a decrease in the melting temperature from 118.92 to 113°C in LDPE–vanillin films. The migration values of modified LDPE–vanillin films remained well within the limits of 10 mg/dm^2, ascertaining its compatibility for food packaging applications.

Compared with plain LDPE, the LDPE–vanillin film has better prospects as a packaging material for solid foods having considerable fat content. The presence of vanilla aroma released by the modified LDPE film in the headspace was further confirmed by GC-MS. Instrumental data corroborated sensory data on odor profiling of the films. Further studies on imparting of vanilla aroma to foods with varying fat content, packaged in LDPE–vanillin, stored under different conditions and evaluated periodically, will be beneficial in exploring the potential of LDPE–vanillin in food packaging applications and its commercialization.

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