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Effect of electrospun montmorillonite-nylon 6 nanofibrous membrane coated packaging on potato chips and bread

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ABSTRACT

Electrospinning technique was used to deposit montmorillonite composite nylon 6 (MMT-N6) nanofibres over polypropylene films. The poor intrinsic Oxygen Transfer Rate (OTR) of polypropylene of 963 cm3/m2/24 h increased to 35 on N6 coating, but significantly increased to 12.5 by coating with montmorinollite incorporated N6. In comparison the Moisture Vapour Transfer Rate (MVTR) of polypropylene of 11.6 g/m^2 24 h was not improved by N6 coating (15.5 g/m^2 24 h) but slightly improved on incorporating the clay to N6 (8.4 g/m^2 24 h).The effect of packaging of potato chips and bread in Test(MMT-N6) and control(polypropylene) was studied. The malondialdehyde levels in potato chips increased by 0.15 in test to 0.95 μM g^{-1} in control packets suggesting lower rancidity of chips in test packets due to less oxygen permeability. Reduction in moisture absorption was 2% in test packets. The shelf life of bread packed in test films increased by 2 days due to inhibition of microbial growth. These effects could be attributed to the improved oxygen and moisture permeability barrier conferred by montmorillonite clay incorporation in the N6 membranes. This is the first report on use of MMT-N6 nanofibrous membrane coating on polypropylene films to extend the shelf life of the food products by preventing lipid peroxidation and microbial growth by reducing oxygen and moisture transfer.

Industrial relevance

Achieving high barrier properties of packaging films is one of the prime goals of food packaging industries for providing longer shelf life to the food product. This study shows an application of electrospinning technique to prepare nanoclay composite fibres coated packaging films having high barrier properties against oxygen and moisture. Application of electrospinning technique provides many advantages for food packaging industry like a very low amount of raw material is required to make uniform coating on substrate, provides choice of wide variety of food grade polymers to prepare composite fibres for various packaging applications, and very simple technique to apply nano range thick coating on the surface of conventional packaging films, which can be exploited in food packaging industry. This study is the first report on application of nanoclay composite fibres for packaging of most commonly consumed food products like potato chips and bread. Potato chips and bread are the prime food products consumed globally and forms major market for packaging industry. Any packaging solution for extension of shelf life of such food products has high significance for food industry.

1. Introduction

Major issues in maintaining the qualities of packed food are oxygen and moisture control. Excessive oxygen concentrations can have deteriorative effects on fats, proteins, food colors, vitamins, flavours, and other food constituents (Lund, Lametsch, Hviid, Jensen, & Skibsted, 2007). Moisture in food influences the appearance, texture, and flavour. It also leads to growth of microorganisms (Huis in't Veld, 1996). Among commonly consumed food items, potato chips and bread are prone to such changes and therefore require packaging solution which prevents permeation of oxygen and moisture.

Globally potato chips are one of the popularly consumed snack food items for people for in-between and during meals (Abong, Okoth, Imungi, & Kabira, 2011). Potato chips belong to a highly competitive and fast growing sector of the food market and demand innovative packaging solutions (Man & Jones, 2000). Moisture absorption, light and oxygen induced rancidity lead to gradual loss of texture, and development of undesirable flavours are invariably observed during the shelf life of potato chips (Arthur, 1991). The ideal potato chip package would thus exclude oxygen, moisture as well as light in order to achieve prolonged shelf life (Arthur, 1991). Currently local vendors mostly use polypropylene for packaging of potato chips which offer shelf life of 2–3 weeks (Arthur, 1991; Man & Jones, 2000).

Bread spoilage has significant commercial impact as it is a staple food all over the world. It is a perishable food with a short shelf life

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because of microbial spoilage. The short shelf life of bread can also result from an excessive drying, which negatively affects its texture but does not favour microbial spoilage. Packaging with lower water vapour permeability can slow down or prevent the drying of bread during its storage period. Shelf life of the product determines its range of distribution. In general for a wholesale distribution system, bread products demand shelf life of minimum 5-days. Bakers who wish to extend their markets are motivated to enhance the shelf life of their product.

Presently food packaging industry depends mainly on plastics, polyethylene, polypropylene, and polyethylene terephthalate materials which have low barrier property against gases and moisture (Duncan, 2011; Weiss, Takhistov, & McClements, 2006). Food packaging is rapidly moving towards development of high barrier properties. Nanotechnology has found wide applications for development of high barrier composite films by incorporating nanoclay in the polymer matrix. The nanoclay (montmorillonite) containing polymer composites are known to have high barrier properties for gases and moisture (Choi, Cheigh, Lee, & Chung, 2011; Zehetmeyer, Soares, Brandelli, Mauler, & Oliveira, 2012; Zehetmeyer et al., 2013). This is because of the tortuous pathway created through the sheet like structures of nanoclay in the film (Bharadwaj, 2001; Bharadwaj et al., 2002; Mirzadeh & Kokabi, 2007; Weiss et al., 2006).

Nanocomposites can be produced using electrospinning (Chronakis, 2005; Dalir et al., 2012). There are many reports on the methodology, structural characterization, morphology, mechanical and thermal properties of electrospun nylon 6 and nanoclay composite (Fong, Liu, Wang, & Vaia, 2002; Li, Bellan, Craighead, & Frey, 2006). However studies on barrier properties for packaging applications have not been reported so far. Therefore it will be of interest to study barrier properties of electrospun montmorillonite composite nanofibrous membrane.

The polymer used for making composite fibres is nylon 6. It is a Food and Drug Administration (FDA) approved food grade polymer and can be easily electrospun. It is one of the widely chosen polymers for developing nanocomposites for various applications including innovative food packaging (Brody, Bugusu, Han, Sand, & McHugh, 2008).

The objectives of the current study are synthesis of montmorillonite composite nylon 6 nanofibrous coated packaging films, study of its barrier properties against oxygen and moisture transfer; and use of such films for packaging of potato chips and bread with respect to effect on moisture absorption, lipid peroxidation and microbial growth.

2. Materials and methods

2.1. Materials

Nylon 6, montmorillonite nanoclay, thiobarbituric acid (TBA), and malondialdehyde bis(diethyl acetal) (MBA) were obtained from Sigma Aldrich. Trichloroacetic acid (TCA), ethanol and petroleum ether were obtained from Sisco Research Laboratory (SRL). Sabouraud's agar and nutrient agar were obtained from Hi-Media. Freshly fried potato chips required for packaging were obtained from local vendor on the day of experiment. Bread used for packaging was commercially available Spencer white bread wast purchased on the same day as per the manufacturing date printed on the packet.

2.2. Preparation of MMT-N6 nanofibrous membrane coated polypropylene films

Polymer solution (MMT-N6) was prepared by mixing 1.9 g of nylon 6 (Sigma) and 0.1 g of montmorillonite clay (Sigma) in 10 g of 98% formic acid and the solution was stirred overnight. For electrospinning, polymer solution was placed in a 2 ml surgical syringe with the needle tip connected to a high voltage supply. The electrospinning was performed by applying high voltage of 30–35 kV and the distance between the tip of the needle and the collector was kept at 10 cm. Collector was 10×10 cm^2 polypropylene sheet (38 μm thick purchased from local vendor) mounted on an aluminium foil. The flow rate was kept constant at 0.1 ml/h controlled by a syringe pump. The coating was performed for 1 h.

Nylon 6 coated polypropylene films were prepared by electrospinning 19% (*w*/*v*) nylon 6 in 98% formic acid nylon 6 polymer solution under similar conditions.

2.3. Preparation of packets for packaging of potato chips and bread

Polypropylene films (38 μm thick) were bought from local vendor and were used to make control packets whereas MMT-N6 coated polypropylene films were used for making test packets such that MMT-N6 coating lies on the inner side of the packets as shown in Fig. 1.

2.4. Characterization of montmorillonite—nylon 6 nanofibres

For studying morphology MMT-N6 fibres were mounted on a carbon grid and SEM image was generated using SEM Quanta 200 FEG achieving resolution of 20,000×. Average fibres diameter was obtained by taking average of 50 fibres using Image J 1.46 software.

To analyse the presence and dispersion of nanoclay in the fibres, a small amount of fibres was coated on carbon coated TEM grids, and mounted on Philips CM12 Transmission Electron Microscope. The accelerated voltage of 120 kV was applied. Electron dispersive X-ray (EDX) technique was used to analyse the presence of nanoclay in terms of elemental constituents like silicon and aluminium. To study the structural properties of montmorillonite clay and nylon 6 in MMT-N6 nanofibrous membrane, XRD analysis was carried out using Bruker D8 Advanced for pure nylon (N6), montmorillonite (MMT), montmorillonite containing nylon 6 nanofibres ((MMT-N6 NF) and nylon 6 cast film with MMT (MMT-N6 cast) using Cu Kα radiation of wavelength 1.5418 A° with step scanning with the size 0.01°. MMT-N6 cast films were prepared by drop casting 0.1 ml of MMT-N6 polymer solution as mentioned in Section 2, on 1×1 cm^2 glass slide.

Further studies were performed to analyse the effect of MMT clay on mechanical behaviour of composite nanofibres. Universal testing machine Ametek Lloyd instrument, LRX Plus was used for analysis of the mechanical properties of MMT-N6 nanocomposite nanofibrous membrane (test) and nylon 6 nanofibrous membrane (control) based upon American Society for Testing and Materials (ASTM D1822, 2013). The cross head speed was maintained at 1 cm/min. Sample size of 5 $\times$ 1 cm^2 was used for the analysis. Light barrier property was studied by measuring percentage transmittance in the wavelength for the range of 200–900 nm for plain polypropylene (control) and nanoclay containing nanofibres coated polypropylene sheet (test) using UV/Vis spectrophotometer (ATI Unicam UV4, Great Britain).

2.5. Barrier properties of MMT-N6 nanofibrous coated polypropylene sheets against oxygen and moisture vapour

Barrier properties of packaging film were analysed based upon the permeability of gases across the packaging film. Permeation is the rate at which gaseous molecule passes through the solid material. Lower permeability indicates higher barrier property of the packaging film. Permeability of oxygen and moisture is reported as oxygen transmission rate (OTR) and moisture vapour transmission rate (MVTR) respectively. OTR studies were carried out using N 500 Gas permeation analyser as per ASTM D 1434-82 (2012). Circular disc of MMT-N6 nanofibres coated, N6 nanofibres coated and non-coated polypropylene sheets having 10 cm diameter and 38 μm thickness was used for analysis. MVTR studies were carried out using Mocon Permatran-W@ 3133 on MMT-N6 nanofibres coated and non-coated polypropylene sheet of size 50 cm^2 and 38 μm in thickness based upon ASTM F1249 (2013). The relative humidity was maintained at 100% during the course of experiment.