Polymer nanocomposites with nanostructured copper flakes for protection as barrier in packaging materials in food industry

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Abstract. Polymer nanocomposites as multilayered and single layer are used as barrier protection for the entry of UV and moisture. Here the polymer nanocomposites with novel nanoflakes are simulated with the optimized geometry of nanoflakes. The barrier properties are verified with the change in width of the dispersed nanoflakes of polymer matrix. The optimization of the copper nanoflakes is investigated and studied using two model with different dimensions of the nanoflakes in the polymer nanocomposite. The diffusivity flux at the interface of air and the polymer matrix varies from $5 \times 10^{-12}$ mol/(m$^2$s) and $4 \times 10^{-5}$ mol/(m$^2$s) for the models proposed.

Keywords: Nanoflakes, Nanopackaging.

1. Introduction
Recent revolutionary changes in the field of nanotechnology intend novel and innovative solutions to all areas of science and technology but very little explored to the food sector industry. The involvement of nanotechnology in biomedical and pharmaceutical applications led to the interventions of nanotechnology in food industry in specific packaging market. The field of nanotechnology is very vast as it is a bottom up approach. The nanostructured systems in food sector include the fabrication and impregnation of nanoparticles, nano emulsions and microemulsions in polymer matrix to have a thick layer as a packaging material hence making it low cost and affordable. The nanomaterials enhance various properties that include solubility, bioavailability, controlled release and biocompatible. Some other features also include food safety, flavoring, coloring and nutritional additives. Nanocomposites with polymer matrix reinforced in nanofillers, nano clay, nanotubes, nanospheres and cellulose fibrils are used in packaging of food products at various stages in the food chain cycle. Several natural and synthetic polymers are extensively used and experimented with the innovative nano dopants to improve the properties. Due to the environmental concerns there is a growing demand for biodegradable packaging to tackle the needs of huge population utilizing it. One of the important properties for inclusion of nano dopants into the polymer matrix in the food packaging is to improve the antibacterial properties with large surface area, size, shape and chemical functionalization. Graphene and CNT based polymer nanocomposites have showed promising results in terms of offering high resistance barrier properties and superior surface area.

2. Materials and methods
Classification of packaging for food industry is broadly classified as Active packaging, smart packaging, improved packaging and biobased packaging as shown in figure 1. Active packaging of food items mainly deal with the improvements in characteristics such as antimicrobial, antioxidant, anti-absorbent and UV exposure. Improved packaging deals with the study and effects of temperature, moisture stability, mechanical strength, durability and stability. In this class of materials for packaging,
the nanomaterials are doped with polymer matrix for gas barrier properties, temperature and humidity. A wide range of nanomaterials are clay nanoparticles with polymers to reduce 80-90% barrier properties for the manufacture of bottles for beer, edible oils and carbonated drinks. Smart packaging is newly trending with the primary focus on intelligent functions that include application towards sensing and indicating the freshness or contaminations in food to monitor the changes in processed and fresh food items.

![Figure 1. Types of Nanopackaging in food Technology](image)

The special characteristic of biodegradable packaging materials is their ability to decay through action of living cells. These biodegradable polymers with nano dopants embedded can be extracted from biomasses as proteins, polysaccharides, and polynucleotides. The problem arises due to the brittleness, low heat distortion generated temperature, high vapor permeability. The application of nanotechnology to these different types can be catered through the improvement in properties and cost effectiveness. Polymer nanocomposites in specific bio nanocomposites are a hybrid form of nanostructured materials with improvised mechanical, thermal and gas barrier properties with a unique feature of environment friendly solution and reduce the usage of plastics as packaging materials. As per the classification as shown in figure 2, the application of nanotechnology and its growth in food Industry is at its initial stages of development but finds possibilities in every aspect of science. There are scientific regulations of nanotechnology in food components which is characterized by effect on the bioavailability and the nutritional value of food. Recent developments and regulations of food nanotechnology is characterized by various uncertainties, one such is risk characteristics. The functionality of food nanotechnology determines the bioavailability and the nutritional value of food. The ultimate parameter in terms of toxic nature of nanomaterials in food packaging depends on physiochemical characteristics and dosage. Safe application of nanotechnology requires extensive characterization and assessment in vitro and in vivo.
Two major concerns of the developing field of food nanotechnology are allergy and heavy metal exposure and release because of the prolonged exposure of nanomaterials on different types of food packaging and hence the health of an individual. This leads to toxic outcomes that cannot be ignored and a lot of study with detailed investigations to be carried out to get a detailed information on the release of heavy metals into food stimulants and their accumulation. This release of metallic ions from the various packed material has the possibility to increase intracellular ROS level.

3. Nanomaterials and Nanostructures in food packaging

Due to the nanometer size particles obtained by dispersion these nanoparticles incorporation will improve the mechanical, thermal, barrier and physio chemical properties. Food packets obtain tensile strength with the process of nano reinforcement. Nano clay is extensively used for this purpose. The main advantage of using nano clay is to increase the barrier of the polymer materials to gas and water. The theory that the clay nanoparticles can shut the permeability as much as 75%. This theory focuses on improved barrier properties through the use of cross linked tortuous lined path in the matrix of clay plates that force the gas to travel a longer distance to diffuse through the fabricated membrane. Here the complete length for the coverage distance is function of high aspect ratio of the clay filler and the percentage of volumetric of the nanofillers in the matrix of polymer. Cellulose is another class of nanomaterials that have very advantageous features of cost effective, light weight and high reliable providing strength. Tensile properties can be improved in several polymers where cellulose is integrated such as polyethylene naphtha late, polyvinyl alcohol, polypropylene and polyamide. CNT and graphene as nano dopants are extensively preferred because of their superior electrical properties of which the dominant is the resistance and hardness. Carbon nanotubes are cylindrical structures with nanoscale dimensions that consist of concentric tubes which is called multiwalled nanotube or one atomic layer thick single walled nanotube. Graphene nanoplates is an uncoiled single walled nanotube. These two nanoparticles have high aspect ratio and their elastic modulus is as high as 1 TPa. The other nanofillers include silver, zinc oxide, titanium dioxide, carbon nanotubes, copper and copper oxides as shown in figure 3. Nanostructured materials find applications in food science sectors where nano sensors and new packaging materials are explored. The nanostructured materials include liposomes, nano emulsions and...
microemulsions that enhance the solubility, bioavailability and protection of bioactive components during manufacture and storage.

![Diagram](image)

**Figure 3.** Nanomaterials and its classification based on nano-object and surface structure

4. **Polymer matrix with Nanomaterials**

Over the past few decades, the use of polymers as food packaging materials is extensively used in food industry due to its numerous advantages over the conventional materials. The polymer industry has increased from 5 million tons in 1950s to 100 million tons as of today with 42% covered by packaging industry.

![Diagram](image)

**Figure 4.** Three types of composites tactoid, intercalated and exfoliated.

With the packaging industry completely relying on polymers itself worth 2% of the gross national product thereby reduction of volumes of waste materials disposed in landfills and contribute to decrease CO2 emissions, Polymer nanocomposites have much better polymer/filler interactions than anyother materials available for packaging of food items. The nonreinforcement techniques with their structure
have increased viability and tensile strength. There are three main polymer clay morphologies tactoid, intercalated and exfoliated. In the tactoid structure polymer chains and the nano clay gallery are immiscible as they have very poor affinity towards each other as shown in figure 4. Polymer based nano clay composites provide high affinity and exfoliated with interlayer space making single and multi-layer sheets. If moderate affinity for the polymer they are classified as intercalated structures.

5. Structure of Nanocomposite for simulation
A low-cost alternative to multilayer packaging is employed based on the structure that contain few weight percentages of nanometer thick platelets of nano clay and dispersed uniformly in the polymer matrix as shown in figure 5. The path length increases throughout the concentration of the nano meter thick layer. The distance travelled by a typical external molecule that include moisture or oxygen is nh/2 where n is the distribution of number of nano clay particles into the matrix and h, as width of the constructed barrier. As the thickness t of the platelet and the spacing between the individual platelets reduces as compared to the platelet width, the volumetric fraction, ϕ of nanofiller is expressed as (nt)/d .

$$C/C_0 = 1$$

$$C/C_0 = 0$$

Figure 5. Idealized morphology for diffusion through polymer nanocomposites containing dispersed nanoflakes

$$d' = d + \frac{nh}{2} = d + \frac{h}{2t} \phi d$$  \hspace{1cm} (1)

Diffusion problem in the nanoflake filled polymer sheets this is avoided by generalizing through assumptions and theories proposed where the drastic changes in diffusivity as a functional component of loading level and the nanofillers aspect ratio. The equation pertaining to this change is as follows.

$$\frac{D_o}{D} = 1 + \frac{(h/t)^2 \phi^2}{4(1-\phi)}$$  \hspace{1cm} (2)

Polymer nanocomposites analysis for various properties of oxygen barrier influenced by configuration, structural parameters including volumetric fraction, improved aspect ratio, and the orientation angle. The finite element model is deployed to design and introspect an ideal nanocomposite for improving the properties of barrier protection. It is described in terms of permeability coefficient of the polymer matrix. The diffusion property of the matrix is mainly influence by two factors structural parameter,
orientation angle and volumetric fraction of the nanoplates of clay. The model proposed describes the diffusion of the gas through flake system as is influenced by tortuosity which is written as

\[ D = \frac{D_0}{\tau} \tag{3} \]

Where \( D \) and \( D_0 \) are the two diffusion coefficients of nanocomposite indicating it for a pure polymer composite. This is carried out in two dimensions 2D and 3D in COMSOL Multiphysics. The angular orientation also has a large influence on the gas barrier properties of the polymer nanocomposite. The tortuosity is the highest when the flakes or the nanofillers are positioned perpendicular to the direction of gas diffusion. The geometry in COMSOL is chosen for a very small area of 0.75 μm × 1.1 μm as shown in Figure 6.

A high density polyethylene matrix is considered for our study with copper nanoflakes. The properties of the materials are considered as in Table 1.

| S. No | Property              | Value       |
|-------|-----------------------|-------------|
| 1     | Porosity              | 1           |
| 2     | Electrical Conductivity | 58.1 × 10^6 |
6. Results and discussion

The nanomaterials properties with values of electrical conductivity, coefficient of thermal explanation, neat capacity at constant pressure, density, thermal conductivity, young’s modulus and poisons ratio. The figure 7. shows the diffusion flux of the membrane with the angle orientation of 900 orientation of the nanoparticles of copper. As we get inset into the 2D polymer nanocomposite package, the diffusion flux variation is from 5 to $30 \times 10^{-12}$ mol/(m²s). The dimensions of the nanoflakes of the copper metal for the simulation is 70 nm in width and 100 nm in height.

The 2D images of the nanoflakes with the arrow directions show the diffusion of air molecules through the polymer nanocomposite as shown in figure 8. It is verified that the first layer of the intercalated and exfoliated layer with the spacing or gap of 50 nm and 70nm along the Z and X direction along the 2 dimensional plane for diffusivity.
Figure 8. Three Dimensional image of multilayers for surface diffusive flux for Model 1

From the 3 dimensional image of figure 9 the multilayers of the nanocomposite is not considered but a single monolayer of the nanoflakes is simulated for its concentration across the layer in one direction for barrier properties and the diffusion constant.

Figure 9. Meshed structure with the cut plane for Model 1

As the cut plane of the plots for that study of diffusion flux and concentration is carried out with a different concentric spheres as shown in figure 9 the diffusion flux changes from $30 \times 10^{-12}$ mol/(m$^2$s) from the previous results to $30 \times 10^{-12}$ mol/(m$^2$s).

Figure 10. Two Dimensional image of diffusion profile along ZX plane for Model 1.
The above figure 10 shows the inset into the cut plane with angle of measurement along the ZX plane. The observed plots show the diffusion profile of the materials at the boundary of the package materials with the nanoflakes of copper clearly depicted.

**Figure 11.** Concentration of moisture along the arc length interface of air and nanodoped polymer matrix for Model 1

The figure 11 that along the length of the membrane ie from the outer side towards the inside where the food will be packed, the concentration of oxygen or moisture molecules reaching to the inner side is very near to a value of 0.5 starting along the y axis with a maximum value of 12 mol/m^3 and hence proves it to be a very good material for protection against moisture and highly diffusive.

**Figure 12.** Average Diffusion coefficient of the model

The diffusivity constant as plotted has values of 0.1×10^{-10} m^2/s to 10×10^{-10} m^2/s as shown in figure 12. There are variations in the plots at around 0.1 um of an area as there is a barrier provided by the copper nanoflake to the incoming gases. The change in the dimensions of copper nanoflakes resulted in variation of concentration and the diffusion flux density. As from the previous observation the length of the
polymer layer doesn’t account much because it is protecting at the initial phase itself so how long is the polymer matrix along the X axis is negligible.

The array of copper nanoflakes for simulation is 7×3 units with a spacing of 70 nm and 100 nm respectively in the two directions of X and Y for width and height as shown in figure 13. The nanostructures are arranged in a single layer and not multilayer. The minimum and maximum surface concentration across the membrane of the polymer matrix is 60×10⁻¹² mol/(m²s).

The arrow in figure 14 shows the direction of diffusive flux with the surface concentration gradient of 6×10⁻⁵ mol/m²s. The tip of the nanostructured nanoflakes at the interface of atmosphere and the inner layers exhibit the most barrier property and offers protection.
As the cut plane of the plots for that study of diffusion flux and concentration is carried out with a different concentric sphere as shown in figure 15, the diffusion flux changes from $6 \times 10^{-5}$ mol/(m$^2$s) from the previous results to $4 \times 10^{-5}$ mol/(m$^2$s).

**Figure 15.** Two Dimensional plot of concentration for Model 2

As can be seen along X-axis the barrier is provided at a distance of 0.05 um away from the outer cover compared to the previous simulation where the barrier protection happened at 0.1um. Hence the rectangular form of nanostructures are appropriate and enhance the barrier properties if they are of appropriate dimensions in terms of nanometer.

The diffusivity constant as plotted has values of $0.1 \times 10^{-10}$ m$^2$/s to $10 \times 10^{-10}$ m$^2$/s as shown in figure 16. There are variations in the plots at around 0.1 um of an area as there is a barrier provided by the copper nanoflake to the incoming gases. 

**Figure 16.** Average diffusion coefficient along arc length for Model 2
Figure 17. Concentration of moisture along the arc length interface of air and nanodoped polymer matrix for Model 2

The figure 17 shows the graph of concentration of moisture that along the length of the membrane i.e. from the outer side towards the inside where the food will be packed, the concentration of oxygen or moisture molecules reaching to the inner side is very near to a value of 0.005 with a maximum of 5.5 mol/m$^3$ along the y axis and hence proves it to be a very good material for protection against moisture and highly diffusion constant.

Conclusions

There is interaction between the polymer matrix and the air interface to investigate the factors influencing the transport mechanism. Diffusion Flux, barrier potential and relative humidity that play key role in the quality of the packaging material for food applications. Novel polymer nano composites-based nanofilms are attractive in the emerging field of packaging food as they improve the barrier properties of gas offering enhanced protection, improved mechanical and thermal resistance with reduced cost of manufacturing and ease of recycling. The addition of nanofillers of copper in the form of nanoflakes to the polymer matrix improved the diffusion flux and barrier potential through simulation of two models proposed. Hence nanocomposites are a promising alternative for food packaging industry. A detailed analysis and its effect of various other nanofillers are crucial to investigate.

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