POLYMER-NANOPARTICLE COATINGS FOR BARRIER FILMS

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Introduction

The addition of inorganic clay nanoparticles to polymers is becoming ever more common due to the enhancement in material properties this can bring. Nanomaterials, with at least one dimension in the 1-100 nm range, have very strong interfacial forces between their domains leading to improvements in mechanical properties [1-3], chemical stability [3-5], and gas barrier properties [6-11].

Depending on the degree of dispersal of the nanoparticle between polymeric chains, the nanoparticle can either be intercalated or exfoliated, or a mixture of both. For exfoliation a complete dispersion or separation of the nanoparticles results in a large number of separated high aspect ratio platelets dispersed throughout the polymer matrix. Such an arrangement is found to be ideal to provide barrier properties to the film where the presence of the nanoparticles causes a lengthening of the diffusion path for any permeating gas molecules due to the increase in the tortuousity of the pathway. In addition the particles also lead to a restriction of the (long) polymer chain reducing the gas diffusion rate through the film. The effect is shown diagrammatically in Figure 1. It has been shown that even small loadings of nanoclays are sufficient to reduce the gas permeability through a polymer [11]. The addition of nanoparticles to the polymer matrix also leads to an improvement in the resultant mechanical properties.

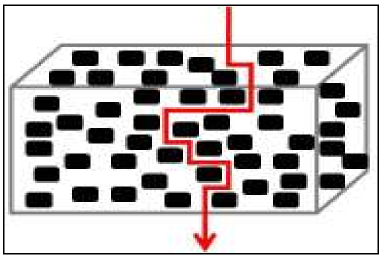


Fig. 1 Inorganic nanoparticles imbedded within a polymer coating act to create a tortuous path for incident air/moisture molecules

This report demonstrates that complete exfoliation of the nanoparticles is possible and good barrier films can be created. In particular it investigates the creation of a new barrier film through the addition of clay nanoparticles to a polymer solution that can be used as a coating layer on a base thin flexible PET film that for example can be suitable for the packaging of, for example, foods, chemicals and pharmaceutical products.

Experimental

The inorganic particles considered were inorganic clay particles which were dissolved together with a polymer in water and then thoroughly mixed at high speed.

The mixed solution was used to make thin film coating layers on poly(ethylene terephthalate) (PET) using a draw-down method.

The coating layer was then dried before oxygen transmission rate measurements (OTR) were made on the film using an OX-TRAN 2/20 from Mocon at test conditions of 23°C and 85 % relative humidity.

After the OTR measurement a JEOL 7400 FEGSEM scanning electron microscope (SEM) was used to analyse the film. Atomic force microscope (AFM) images were taken on further areas of the sample film (without a carbon layer) using a Digital Instruments (Veeco) Dimension 3000.

Results and Discussion

For all solutions, mixing of the polymer and inorganic clay particles was performed for a number of hours, and typically overnight. The shear forces produced during the mixing process acted caused the clay platelets to undergo aggregation and exfoliation in the dispersed solution. In all cases the final particle size was small enough to give a transparent coating layer with no optical effects when applied to the PET substrate by use of a draw-down method.

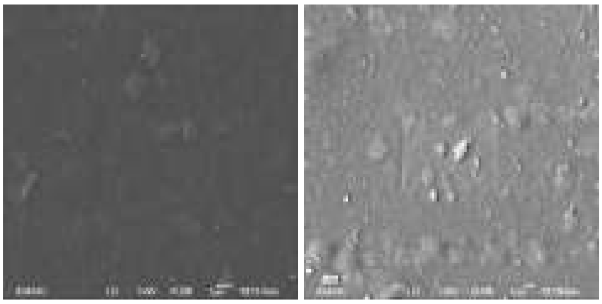
To investigate the effect of the clay and polymer concentration on the resultant barrier properties, measurement of the oxygen transmission was made on a number of solutions containing varying concentrations of both components.

For barrier solution **A**, low concentration clay and polymer solutions were thoroughly mixed together at high speed. The final solution was used to produce a barrier film coating on a base PET substrate with a coating weight of 0.74 gsm. For this film an OTR value of 25.6 cc/m^2-day was measured, which is considerably greater than a value of 10 cc/m^2-day that can be considered to provide an acceptable barrier for food products.

An SEM image of an area of barrier film **A,** that had first been coated with a monolayer of carbon, taken at a magnification of x7,000 using an incident beam voltage of 3 kV and beam current of 10 μA, is shown in Fig. 2(a). An

AFM image was also taken on a non-carbon coated portion of the film with a 5 µm scan shown in Fig. 3(a).

For these images the particles shown can be measured to have dimensions of around 1 µm by 1 µm indicating the mixing process has acted to break up the inorganic clay particles. The SEM image shows that in this case the process has given a partially exfoliated film where some of the particles still remain intercalated. Consequently the barrier properties of the film, while reduced would not be sufficiently low enough to be used in applications such as for the packaging of food.

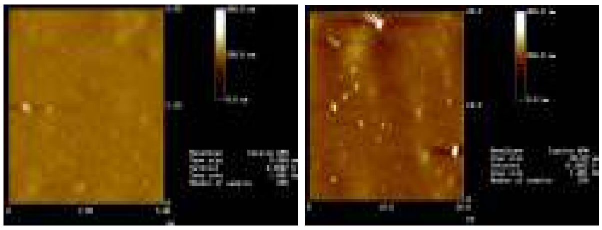


(a) (b)

Fig. 2 Scanning electron micrograph images of (a) partially exfoliated film, and (b) fully exfoliated film

For barrier solution **B**, the polymer and clay were mixed at high speed with both components at high concentration. After mixing the solution was then diluted to a low concentration for making the film. The resultant coating weight of the film was 0.55 gsm and was thus less than that of film made from solution **A**. Despite this, the barrier solution **B** film gave an excellent OTR value of 9.4 cc/m^2-day. For this barrier film the low OTR value obtained can be explained to have arisen from a complete exfoliation of the inorganic nanoparticles; this is shown in the SEM image of Fig. 2(b), and the 20 µm AFM scan shown in Fig. 3(b).

For this SEM image, a portion of the film was considered at a magnification of x4,000 from an incident beam voltage of 3 kV and beam current of 10 µA. Unlike in the partially exfoliated image, this film now has a large number of particles distributed fully and evenly across the entire film surface. While as previously there are a number of 1 µm sized particles here there are also a large number of smaller particles present. This change in film composition can be attributed to the change in the preparation conditions. For this film where there were such a large number of particles present, incident gas molecules would be greatly restricted in their ability to pass through the film thereby leading to the barrier effect observed.



(a) (b)

Fig. 3 Atomic force micrograph images of (a) partially exfoliated film, and (b) fully exfoliated film

Conclusion

This paper has considered the effect of including inorganic impermeable nanoparticles within a polymer matrix for use as a barrier film coating on PET substrates. The results have shown that by carefully and thoroughly mixing at high speed both components together, the shear forces produced can be sufficient to produce exfoliated clay inorganic particles in a polymer matrix. This has been observed through SEM images of the films. Consequently we have obtained barrier film coatings where the OTR values obtained were less than 10 cc/m^2-day. The achievement of effective barrier films to both air and moisture would have a major application for packaging, and in particular for the packaging of food. Where by eliminating or reducing the absorption of oxygen and water the degradation of the contents is prolonged and thus the shelf-life of the contained food can be considerably extended, thereby reducing spoilage and wastage.

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