NANOCOMPOSITES STUDY OF ETHYLENE CO-VINYL ALCOHOL AND MONTMORILLONITE CLAY

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Abstract

Nanocomposite films were investigated for an ethylene co-vinyl alcohol (EVOH)/clay system to determine the interaction between the polymer and the nanoclay and the effect of the nanoclay on the film properties. EVOH and montmorillonite clay at 5% loadings were compounded using a twin-screw extruder. Subsequently, these formulations were further processed into blown films using a twin-screw extruder with various processing parameters. The morphological, mechanical, thermal and barrier properties of the films were examined. The delamination and dispersion of the clay improved in the blown films compared to the compounded material. Young's modulus was found to increase significantly for the nanocomposite compared to the pure EVOH. Oxygen transmission rates were found to decrease as a result of incorporation of the nanoclays. With improved barrier properties, these may potentially be incorporated into military ration packaging systems in order to meet shelf life and survivability requirements.

Background

Nanocomposites containing small amounts of clay (1-5%) have been shown to yield large improvements in barrier properties, as well as in physical properties such as tensile strength, tensile modulus and heat distortion temperature.[1-4] A doubling of tensile modulus and strength without a sacrifice in impact resistance has been achieved for nylon 6/clay nanocomposites containing as little as 2 wt. % of clays. [1,5]

The clay commonly used in these nanocomposites is organically modified montmorillonite, a mica-type silicate, which consists of sheets arranged in a layered structure. Nanoclays are used due to their high cation exchange capacity and its high surface area, approximately 750 m^2/g and large aspect ratio (larger than 50) with a platelet thickness of 10 Å.

The large aspect ratio of the silicate layers has many benefits for several polymeric applications. The interface between the tremendous surface area of the clay and the polymer matrix minimizes the chain mobility, creating a reinforcement effect. In addition, this interface facilitates stress transfer to the reinforcement phase, thus improving physical properties such as tensile strength and tensile modulus [1,5]. Because the nanoclays contain so many individual particles in a relatively small amount of material, it takes low levels of loading (1-5%) to obtain a high concentration of constrained areas within the polymer [6]. More importantly for food packaging applications, these high aspect ratio nanolayers force gas and water molecules to follow a more tortuous path in the polymer matrix around the silicate layers. This results in much larger diffusion distances, thereby lowering permeability [1].

Nanocomposites with these enhanced properties would be ideal for packaging applications. EVOH, a polymer currently used in the packaging industry, was selected for this study because it has exceptional barrier properties and is already being considered for a military food tray. Triton Systems, Inc. is currently evaluating the use of EVOH nanocomposites in these food trays under an SBIR research program. [7]

EVOH is a random copolymer of polyvinylalcohol (PVOH) and polyethylene and is, therefore, less hydrophilic than PVOH. Its properties depend on the ethylene vinyl alcohol composition ratio. EVOH with an ethylene content of 44% exhibits good mechanical properties. (Young's modulus = 2062 MPa; tensile strength = 58.87 MPa; elongation = 280%) and excellent oxygen barrier properties (oxygen transmission rate = 31.00 $cm^3 \cdot mil/(m^2 \cdot d)$).[8,9] However, EVOH is sensitive to moisture which can render itself unsuitable for certain applications. Consequently, the military polymeric tray is being developed with a nanocomposite of EVOH sandwiched in between polypropylene. In this study, films of the

EVOH/nanoclay are studied for military food packaging applications. These polymer nanocomposites are processed into films and evaluated by transmission electron microscopy, thermal analysis, mechanical and barrier properties to compare to the pure EVOH and to determine the effect of clay on this system.

Experimental

Materials

Commercially available EVOH (EVAL® E-105 series) pellets provided by Eval Company of America was used for this investigation. The organoclays were synthesized by Triton Systems or provided by Southern Clay Products, under the trademark Cloisite.

Processing

The organoclays at 5% loading were compounded with EVOH using a Zenix ZPT-30 30mm co-rotating twin screw extruder using a standard mid shear configuration for additive blending. Temperature was varied across the nine zones from 165°C in the feed section to 205°C at the die. Extruded strands were pelletized for secondary processing.

Film samples were prepared by extrusion, using both melt cast and blown film processes. The cast film was processed using a C.W. Braebender Plasti Corder single screw extruder with a 8" film die. The blown film was produced using a Haake® Polylab twin-screw extruder. The screws were conical, counter–rotating and intermeshing with a diameter of 31.8 mm and a length of 300mm. Screw speed was 100 rpm and processing temperatures in zones 1-3 were 160, 205 and 205°C, respectively, and the die was set at 210°C. The die has an interior diameter of 24 mm and outer diameter of 25 mm with an adjustable ring gap.

Characterization

The morphology of the nanocomposites was determined by transmission electron microscopy (TEM). The samples were prepared in a mixture of epoxy and hardener to enable slicing of the samples in the ultra-microtome, using a diamond knife. The microtomed samples were then observed under Philips EM400 Transmission Electron Microscope at 120kV at various magnifications. Tensile properties were evaluated with an Instron® 4200 series instrumentation in accordance with ASTM D882. The load cell was 50 Kg and cross head speed was 2.0 mm/min. Rectangular samples with a gauge length of 2 inches were used. Each result was based on the average of 10 replicates. Measurements were made in both the machine and radial directions.

All samples were processed and then stored in plastic containers at room temperature and ambient conditions.

Differential Scanning Calorimetry (DSC) was used to evaluate the melting and crystallinity of the EVOH in the pure EVOH films as well as the nanocomposite. A Perkin Elmer DSC-7 at a scan rate of 20°C/minute from -50 to75°C was used for the thermal experiments.

Thermogravimetric analysis (TGA) was used also to determine the thermal stability. A TA instrument TGA 2190 was used from ambient to 700° at a can rate of 20°C/minute.

Oxygen transmission rates (O_2TR) were established in accordance with ASTM D3985 using the Mocon® Ox-tran 2/20 at a temperature of 23°C and 50% RH.

Results and Discussion

Morphology

It has been well established that the surface treatment of the nanoclay has a significant effect on the degree of dispersion within the polymer matrix [1,6,10]. TEM results of this study demonstrate that the processing conditions also have an effect on clay dispersion. Figure 1 shows the TEM of the melt compounded EVOH/clay pellet having large clay aggregates with minimum exfoliation of the platelets.

Figure 2 shows the TEM for the cast film displaying some improvement of the dispersion and the orientation of the platelets. While the platelets are not completely exfoliated, the apparent density of clay in the image is higher, indicating improved dispersion.

The TEM for the extrusion blown films processed at 100 rpm in Figure 3 shows that there is an alignment of the clay platelets not visible in the other samples, which is due to the shear forces and biaxial orientation encountered during the blown film process. However, the clay density is similar to the cast film, which is also a shear force process. Shear intensity and processing conditions within an extruder have been reported to have an impact on delamination and dispersion [3]

Mechanical

Table I shows the tensile properties of pure EVOH and of EVOH/clay in the machine direction. The incorporation of clay into EVOH resulted in a significant increase in all tensile properties, as compared to pure EVOH. The Young's modulus of the nanocomposite showed an improvement exceeding 100%, as compared to pure EVOH. The tensile strength of the nanocomposite showed an improvement of 125%, as compared to pure EVOH.

Toughness and per cent elongation also showed improvement in the nanocomposites, however, due to excessive deviation, further investigation is on-going.

Barrier

The incorporation of clay into EVOH resulted in a significantly decreased O_2TR for the nanocomposite, as illustrated in Figure 4. The reduction in O_2TR is typically attributed to the more tortuous path that the gas molecules must travel around well-dispersed platelets of high aspect ratio [1]; however, in this case the clay density and alignment of the clay particles can also contribute to the barrier improvement.

Thermal

The DSC results of the nanocomposite showed that the onset of EVOH melting did not vary significantly from the pure polymer. The melting onset occurred at 153°C and 155°C for the blown film nanocomposite and EVOH respectively. The peak maximum was 166°C. The area under the melting curve was 58 J/g for the nanocomposite and 74 J/g for the pure EVOH indicating that the nanoclay did interact with the polymer to reduce its crystallinity. The opposite was expected with the nanoclay acting as a nucleating agent enhancing crystallinity and therefore contributing to barrier properties.

The TGA data of weight loss as a function of temperature is shown in Figure 5. The EVOH/nanoclay nanocomposite initially loses 2% of its weight at 265 versus 295°C for the pure EVOH. This indicates that the EVOH pure is more thermally stable and that the nanoclay somewhat reduces the stability of the nanocomposite.

Conclusions

Polymer/clay nanocomposites have been developed using EVOH. TEM analysis confirmed that dispersion was attained in cast film and further dispersion was attained in blown film.

Property improvements were observed in tensile strength, Young's modulus, and oxygen transmission rate. The barrier improvement was exceptional, and further investigation of this system is underway with testing being performed at different humidities and temperatures.

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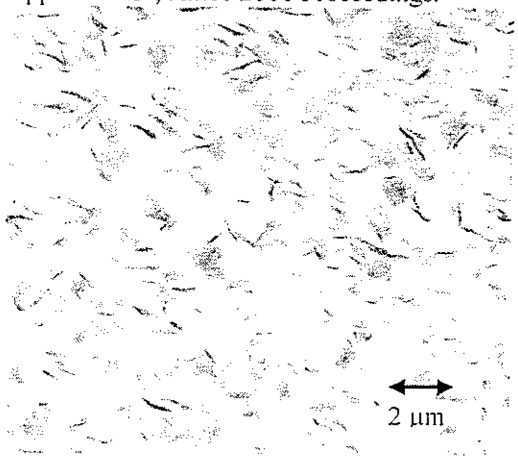

Figure 1. Transmission electron microscopy (16,000X) of nanoclay filled EVOH extruded pellet

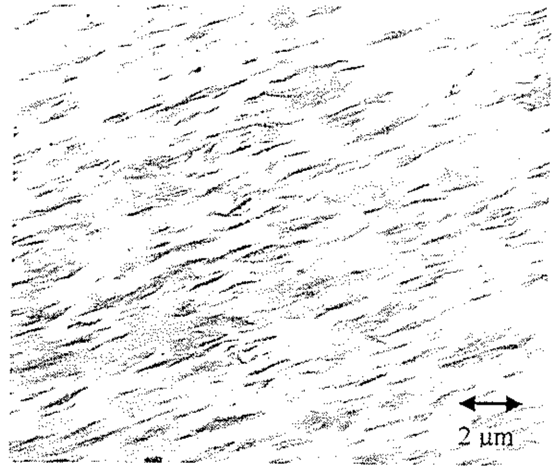

Figure 2. Transmission electron microscopy (16,000X) of nanoclay filled EVOH cast film.

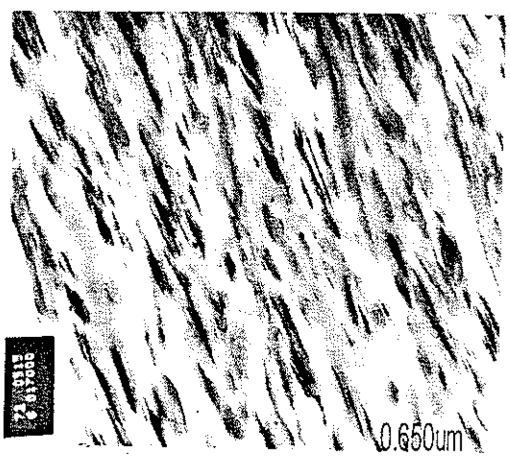

Figure 3. Transmission electron microscopy (17,000X) of nanoclay filled EVOH blown film.

Table 1. Tensile properties of EVOH/clay nanocomposite in machine direction

	Tensile Strength (MPA)	Modulus (MPA)
Pure EVOH	20.4 ±2.4	1080±178
EVOH/Clay	45.9±3.5	2350±331

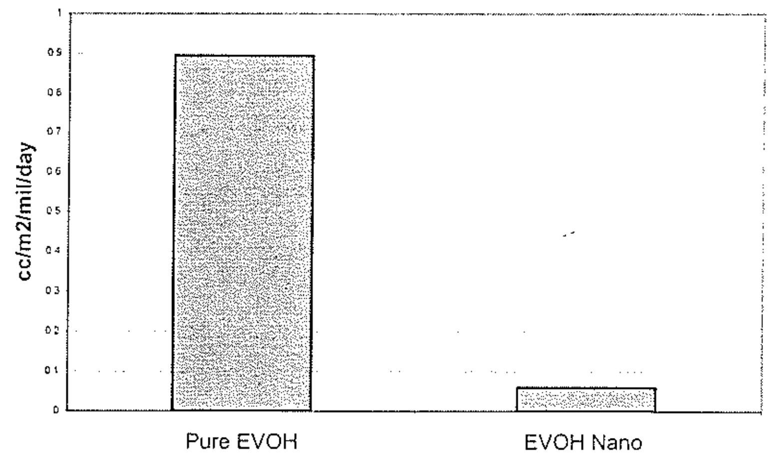

Figure 4. O_2TR of Pure EVOH and EVOH/clay nanocomposite.

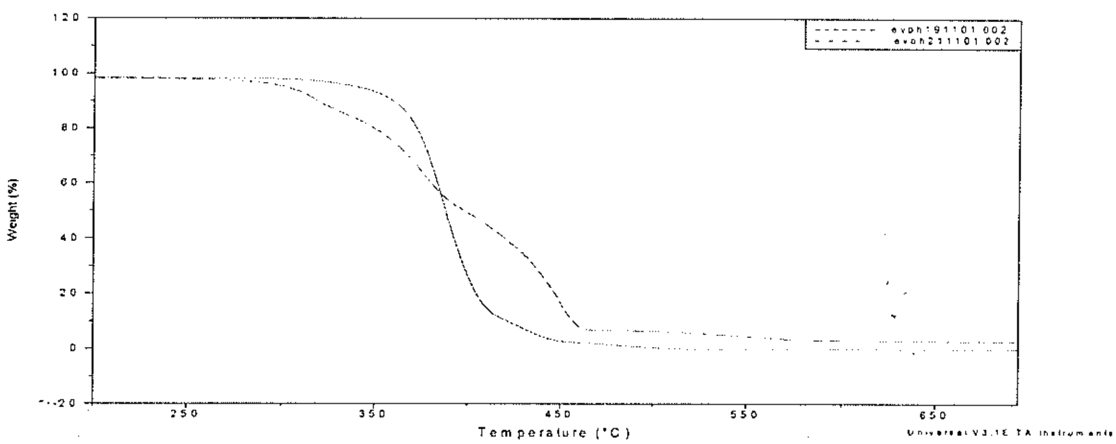

Figure 5. TGA data of EVOH and EVOH/clay nanocomposite.

Keywords: nanocomposite, ethylene vinyl alcohol, montmorillonite