A Study of Barrier Properties of LDPE Nanocomposite Films Under Extreme Environmental Conditions

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Pure and nanoclay (montmorillonite layered silicates, MLS) embedded within low density polyethylene (LDPE) composite films were tested under extreme environmental conditions (i.e. conditioned air of varying temperature-relative humidity combinations: 10°C and 90% RH, 40°C and 20% RH, and 40°C and 90% RH) to determine the effects of nanoclay expansion on water vapor barrier properties. Results from Differential Scanning Calorimetery (DSC) and Thermogravimetric Analysis (TGA) confirmed that the presence of nanoparticles (MLS) within LDPE films increased the thermal quality and stability of the films. A 19 day moisture stability study using nine salt solutions that range between 11.3% to 93.6% relative humidity indicated that the presence of nanoclay particles (MLS) and relative humidity did not negatively impact the hygroscopic (water vapor) barrier properties of the films. The characterization study identified temperature as the primary variant affecting the enhancement and diminishment of water vapor barrier properties. N2 films (MLS embedded LDPE films of 2 mil thickness) of the characterization study showed an increase in the average MLS platelet lengths as temperatures decreased, and N6 films (MLS embedded LDPE films of 6 mil thickness) of the characterization study showed an increase in the average MLS platelet lengths as temperatures increased. Scanning Electron Microscopy (SEM) imaging was the technique used to confirm morphology and nanoparticle (MLS) expansion.

Motivation

More than 46 million MRE (Meal-Ready-to-Eat) packaging films are used to store the food ration consumed by United States military personnel. The MRE packaging films are, however, non-recyclable, because they are foil-laminated films. Thus, close to 15,000 tons of waste is generated annually from this packaging material [4]. This enormous amount of packaging waste has become a national waste concern and has led to the study of nanocomposite films as an alternative packaging solution. In order for the nanocomposite films to be as effective in storing military food rations, it must be able to match the superior water vapor barrier properties of MRE packaging films, and also retain a minimum shelf-life of 3 years at 80°F (required of all MRE packaged foods).

The nanocomposite film that has demonstrated the most promise as an effective alternative to the MRE packaging film is low density polyethylene (LDPE) embedded with low loadings (7.5% by weight) of organically modified montmorillonite layered silicates (MLS) [4]. The dispersion of MLS platelets within the LDPE film creates what is termed an intercalated morphology or complex micro-structural diffusion pathway [2]. The intercalated morphology and tortuous pathway of this MLS/LDPE film limits oxygen and water vapor permeability, thereby, increasing the shelf-life of the packaged contents [2]. Further development of these nanocomposite films will ultimately lead to a packaging product that is biodegradable, recyclable, and microwavable.

A direct correlation has been found between the microstructure of MLS/LDPE and its barrier properties in that the greatest property improvements were seen in exfoliated systems, where clay layers had fractured and dispersed evenly into the polymer matrix [3]. Studies have shown that the barrier properties of MLS/LDPE films are compatible with those of MRE packaging materials in moderate environmental conditions (temperature of 23°C and relative humidity of 50%) but not in extreme environmental conditions [6]. However, military personnel (mainly soldiers) often have to fight battles in extreme environmental conditions (such as the unstable temperatures of the Iraq desert). This implies that the barrier properties of the developed MLS/LDPE must be able to withstand these extreme environmental conditions.

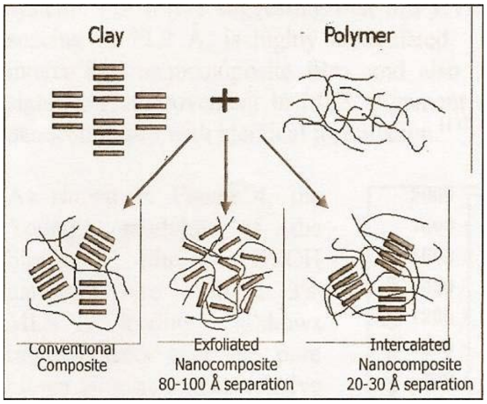

Figure 1: Nanocomposite Morphologies [2]

Question and Hypothesis

Therefore, the experimental question that is investigated in this study is whether the microstructure of MLS embedded LDPE films changes when exposed to extreme environmental conditions and whether these changes influence the barrier properties of the films.

It is hypothesized that the microstructure of the MLS embedded LDPE films will exhibit great water vapor barrier properties under extreme environmental conditions.

Experimental

Materials

The nanocomposite MLS/LDPE films and pure (unmodified) LDPE films used in this study were obtained from the United States Army Natick Soldier Research, Development, and Engineering Command Center in Natick Massachusetts. Details of the processing and manufacturing of these films can be found in Culhane et al. (2005) Films were processed into 2 mil and 6 mil thicknesses. Since the main objective for the development of nanocomposite films such as MLS/LDPE is to replace the MRE packaging film, the use of MRE packaging films provided a necessary control for experimentation. The MRE packaging films were also obtained from the United States Army Natick Soldier Research, Development, and Engineering Command Center in Natick, Massachusetts.

Thermal Analysis Study

The thermal analysis study was carried out using the Differential Scanning Calorimeter (DSC, Q200 Model, TA Instruments, Inc., New Castle, DE) and the Thermogravimetric Analyzer (TGA, Pyris 1 Model, PerkinElmer, Inc., Shelton, CT). The first phase of the thermal analysis study involved the use of DSC to determine the melting points of various pure and MLS embedded LDPE films. Approximately 3 to 4 milligram samples of pure and MLS embedded LDPE films were prepared and then evaluated by the DSC in a nitrogen atmosphere at a rate of 10°C/min within the temperature range of 35°C to 220°C. Thermograms from the DSC were analyzed using the software (TA Universal Analysis) provided by the manufacturer of the DSC. The TGA was used to obtain the degradation (onset) temperatures of the films. Approximately 5 to 6 milligram samples were prepared and then evaluated by the TGA in a nitrogen atmosphere at a rate of 20°C/min within the temperature range of 35°C to 700°C. Thermograms from the TGA were analyzed using the software (PerkinElmer Data Analysis) provided by the manufacturer of the TGA. All thermal analysis experiments were carried out in duplicates.

Moisture Stability Study

Before experimentation, the initial moisture contents of the films were obtained by the oven method. This involved placing 1.5” x l.5” samples of the films in an oven (Model No. OV35245, Thermolyne Corporation, Dubuque, IA) set at a temperature of 103°C for 4 hr. The percent ratio of the loss weight of the film to the original weight of the film was taken as the initial moisture content of the film in percent wet basis.

Moisture stability of the films was carried out by exposing the films to nine relative humidity environments (11.3% to 93.6%) at a temperature of 25°C. The relative humidity environments were obtained by preparing nine saturated salt solutions (representing environments of different relative humidities-Table 1) in a desiccator. Approximately 1.5” diameter films were prepared, weighed, and placed in the desiccators containing the saturated salt solutions. To ensure that the films did not contact the solutions, they were placed in Petri dishes, and the Petri dishes were placed on a perforated support plate that sat about 3 mm on top of the salt solutions. The nine desiccators and contents were placed in an environmental chamber (Model ESL-2CA, ESPEC, FOB Byron Center, MI) to ensure that the desired 25°C environmental temperature was maintained throughout experimentation. After the 19 days, the weights of the films were recorded and used to calculate the moisture contents of the films after being exposed to the various relative humidity environments.

Table 1: Saturated Salt Solutions for Moisture Stability Study

Saturated Salt Solution	Water Activity (aw)*
Lithium Chloride	0.113
Potassium Acetate	0.225
Magnesium Chloride	0.328
Potassium Carbonate	0.432
Magnesium Nitrate	0.529
Cobalt Chloride	0.618
Sodium Chloride	0.753
Potassium Chloride	0.843
Potassium Nitrate	0.936

*aw = relative humidity/100

Characterization Study

The aim of the characterization study was to examine the changes in the microstructure/ morphology of the MLS/LDPE films as a result of being subjected to extreme environmental conditions. Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) were used in the characterization study. The FTIR study was used to identify the presence of montmorillonite layered silicates (MLS) within the low density polyethylene (LDPE) film. A l cm x 1 cm sample of the MLS/LDPE nanocomposite film was cut, and then scanned by the FTIR spectrometer (Spectrum 100, PerkinElmer, Shelton, CT). Peak analysis was then conducted using PerkinElmer's Spectrum analysis programming. For the SEM study, pure and MLS embedded LDPE films were cut into three sets of 1 cm x 1 cm squares and exposed to three temperature-humidity environments: 40°C and 90%RH, 40°C and 20%RH, and 10°C and 90%RH. Temperature-humidity environments were made possible with the use of two air-tight chambers (1.8 m x 0.9 m x 0.9 m) supplied with conditioned air from a temperature-humidity conditioner (Model AA-5460, Parameter Generation and Control, Inc., Black Mountain, NC) and the ESL-2CA temperature-humidity chamber (ESPEC, Inc., FOB Byron Center, MI) [6]. After 72 hours of exposure, samples were coated with gold using a sputter coater (EMS 550X, Electron Microscopy Science, Fort Washington, PA). After gold coating, SEM (EVO 50 Extended Pressure Scanning Electron Microscope-EPSEM, Zeiss, Jena, Germany) imaging was conducted at an accelerating electron beam voltage of 10kV.

Results and Discussion

Thermal Analysis Study

Based upon Carnelley's Rule of organic chemistry, a definite association between melting points and molecular stability can be assessed. Carnelley's Rule states that high molecular symmetry is associated with high melting points [1]. Table 2 shows that although the melting points of the films are different, they are within a range of 1.9°C. Therefore, it can be inferred based upon Carnelley's rule that the films have similar molecular symmetry and stability. In addition, the higher melting points of the nanocomposite films were an indication that the addition of MLS enhanced the thermal stability of LDPE films.

Table 2: Melting Points of Thermal Analysis Study

Sample	Melting Point
MRE	110.7°C
P2	110.6°C
N2	111.2°C
P6	110.6°C
N6	112.5°C

*N2 (MLS embedded LDPE of 2 mil thickness), P2 (pure LDPE of 2 mil thickness), N6 (MLS embedded LDPE of 6 mil thickness), P6 (pure LDPE of 6 mil thickness.

The TGA trial also showed that the films have different degradation (onset) temperatures (Table 3). Because all films (pure and MLS embedded LDPE of 2 and 6 mil thicknesses) have degradation temperatures similar to that of the MRE film, it can be inferred that they are all are as thermally sufficient.

The higher degradation temperature values noticed in nanocomposite films indicated that the presence of MLS enhanced thermal stability by increasing the degradation temperatures.

Table 3: Degradation Temperatures of Thermal Analysis Study

Sample	Degradation Temperature
MRE	439.8°C
P2	473.2°C
N2	499.7°C
P6	456.8°C
N6	496.7°C

Moisture Stability Study

Results from the moisture stability study showed that moisture content of the films did not change more than 1%. The relatively constant moisture content of the MRE film [Figures S3 and S4] was an indication of its superior water vapor barrier properties when exposed to extreme relative humidity environments. The moisture contents of both the 2 mil and 6 mil pure and MLS embedded LDPE films, however, substantially increased when exposed to relative humidity of 93.6%. This is an indication of the loss in water vapor barrier quality of these films in high humidity environments. The 6 mil nanocomposite sample (N6) absorbed more moisture than the 6 mil pure LDPE sample (P6). There was no observable difference between the moisture absorbed by the 2 mil nanocomposite sample (N2) and the 2 mil LDPE sample (P2). In addition, a comparison of the 2 mil samples to 6 mil samples showed that the 2 mil samples absorbed more moisture than the 6 mil samples. However, since the changes in moisture content of the film samples are very small (<1%), this moisture stability study confirmed that the presence of nanoclay particles (MLS) will not adversely affect the stability of the films during exposure to environmental conditions less than relative humidities of 93.6%.

Characterization Study

Figure S1 shows the spectra of the pure LDPE (blue) and the MLS embedded LDPE (black) films. The spectra for both films are essentially identical except for the third peak at a wavelength number of 1049 cm^{-1}. Further literature searches showed that this wavelength number was within the range of the peak wavelength numbers for clay [6]. The FTIR spectra study, therefore, confirmed the presence of nanoclay (MLS) within the nanocomposite film sample.

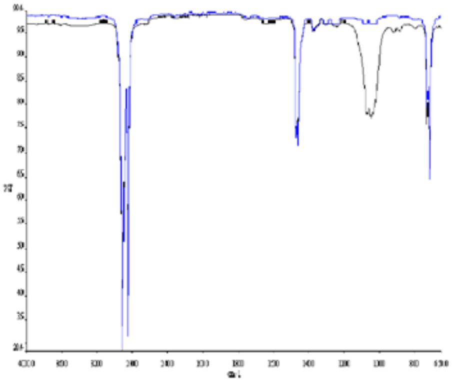

Figure 2: FTIR- Spectra of MLS (1049 cm^{-1}) within LDPE

Because manufacturing pre-determines the fixed morphology and displacement of nanoparticles (MLS) within LDPE, there only exist the potential for the nanoparticles to expand or contract when exposed to extreme environmental conditions. During the manufacturing process, the MLS platelets dispersed within LDPE range from 100 nm to 200 nm lengths [2]. Table 4 shows the average MLS platelet lengths of 2 mil (N2) and 6 mil (N6) nanocomposite films after exposure to extreme environmental conditions (10°C and 90% RH, 40°C and 20% RH, and 40°C and 90% RH).

Table 4: MLS Average Platelet Lengths (nm) after Exposure to Extreme Conditions

Sample	10°C/ 90%RH	40°C/ 20%RH	40°C/ 90%RH
N2	251	178	176
N6	154	214	228

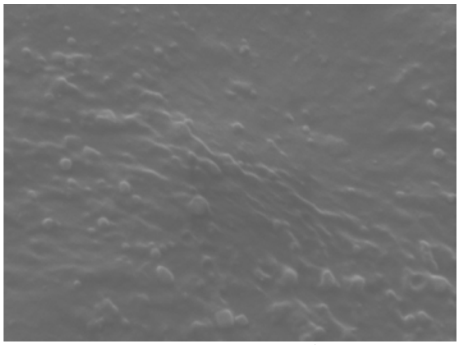

Figure 3: SEM N6 Image at 40°C and 20%RH.

Increasing relative humidity at a constant temperature of 40^{o}C resulted in no significant change in the size of MLS platelets for N2 or N6 films. This finding confirms the results from the moisture stability study that showed that relative humidity environment less than 93.6% did not result in significant changes in moisture contents of the films. In addition, it is suspected that as the platelets were expanding from exposure to high humidity, they were also drying from exposure to high temperature. In contrast, when the humidity was held constant and the temperature was reduced, the size of the platelets increased for N2 but reduced for N6. The result of N2 platelets to increase in size is expected based upon documented studies that relate the effects of water activity and temperature on moisture content and expansion of organic materials such as MLS [7]. The response of N6 platelets to reduce in size cannot be explained. Results indicated that the best water vapor barrier properties were seen in N2 films exposed to lower temperature environments and N6 films exposed to higher temperature environments. When MLS platelets expand, there will be smaller pathways between platelets for gas flow, thereby, leading to improved water vapor barrier properties of the films.

Conclusion

The thermal analysis study using DSC and TGA trials confirmed that the presence of nanoparticles within LDPE films increased the quality and thermal stability of the films. The moisture stability study confirmed that the presence of nanoclay (MLS) and relative humidity did not negatively impact the hygroscopic (water vapor) barrier properties of the films. The characterization study identified temperature as the primary variant affecting the enhancement and diminishment of water vapor barrier properties. N2 films of the characterization study showed an increase in the average MLS platelet lengths as temperatures decreased, and N6 films of the characterization study showed an increase in the average MLS platelet lengths as temperatures increased. No finite trend can be assessed as a result of the characterization study and further experimentation using a wider array of temperature-humidity combinations and other imaging techniques such as TEM will be needed to further verify and quantify results.

The hypothesis of this experiment states that the microstructure of MLS embedded LDPE films will exhibit great barrier properties under extreme environmental conditions. I found this hypothesis to be false in regards to the moisture stability study in which the presence of MLS had no adverse affect on the stability of the films exposed to environmental conditions of relative humidities less than 93.6%. The characterization study implied that this hypothesis was partially true in regards to temperature serving as the primary variant that affected MLS platelet lengths (and nanoparticle expansion), which will consequentially limit water vapor permeability.

This experiment provides plausible results that suggest certain inclinations to food and possibly drug storage applications. Results from this experiment can aid scientist and engineers in designing MLS-embedded LDPE films for long term food and drug storage applications for use in extreme environmental conditions.

Acknowledgements

I would first like to thank and acknowledge God for blessing me with the opportunity to partake in this summer research experience. I would like to thank Dr. Oladiran Fasina for all of his patience, guidance, and support. Thanks to the United States Army Natick Soldier Research, Development, and Engineering Command Center for their donation of film samples. A special thanks is noted to Dr. Michael E. Miller for all of his efforts in helping me to assess imaging data. I would also like to thank the program directors, Drs. Mark Byrne and Steve Duke, for making this research experience socially and academically stimulating. This research was supported by the National Science Foundation (Research Experience for Undergraduates Site Award CHE-0552557). MTN was an NSF REU Fellow.

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