MULTILAYER FILMS OF ETHYLENE CO-VINYL ALCOHOL NANOCOMPOSITE AND POLYPROPYLENE FOR FOOD PACKAGING APPLICATIONS

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Abstract

Retort is a high temperature sterilization process that is used to prolong the shelf life of military rations. Ethylene co-vinyl alcohol (EVOH) /montmorillonite layered silicate (MLS) nanocomposites were co-extruded with retort grade polypropylene (PP) into a multilayer cast film to determine if the addition of MLS to EVOH improved barrier, mechanical, thermal and retort properties. The PP/EVOH-MLS/PP structure showed an improvement in some properties such as water vapor transmission rate, Young's modulus, and seal strength before retort in comparison to the PP/EVOH/PP structure; however, the improvement in properties was lost after the retort process.

Introduction

The packaging for the military's ration, the Meal, Ready-To-Eat (MRE), has stringent performance requirements which must be met in order for the food to maintain quality and nutrition. The MRE must have a shelf life of three years at 27°C or six months at 38°C. [1] The military specification requires that the oxygen transmission rate (OTR) of the packaging must not exceed 0.06 cc/m²/day and the water vapor transmission rate (WVTR) must not exceed 0.01 g/m²/day. Also, the MRE food pouches are retorted at 121°C (250°F) for 30 to 60 minutes, which are the typical conditions required to kill microorganisms and sterilize the contents. [2, 3]

In order to meet the military performance specification, a foil laminate structure is currently used in the MRE food pouch. However, current research is investigating alternative multilayer polymeric packaging structures. [4, 5] Ethylene co-vinyl alcohol (EVOH) is one polymer that is being researched. EVOH is a crystalline, random copolymer of ethylene and vinyl alcohol. EVOH is known to be a superior barrier to oxygen; however the barrier properties of EVOH diminish as the humidity increases. Also, the hydrophilic nature of the material becomes a problem with retort packaging applications because the process requires water and steam for sterilization. EVOH resins absorb moisture as a function of humidity and temperature, decreasing the barrier properties of the resin during the retort process. EVOH experiences "retort shock" which causes an irreversible decrease in barrier properties. EVOH is commonly used for many packaging applications, including PP and EVOH retortable barrier sheet for thermoformed packaging. [6]

Nanocomposites of EVOH and organically modified montmorillonite layered silicates (MLS) are investigated to improve the barrier properties of the EVOH. MLS is a layered silicate commonly used in polymeric nanocomposite systems due to its high cation exchange capacity, high surface area (around 750m^2/g), and large aspect ratio (greater than 50) with a platelet thickness of 10 Å. [7]

The retort grade of PP is also being investigated with the EVOH and/or EVOH/ MLS in a multilayer structure. The PP serves several purposes; it provides protection from water molecules for the hydrophilic EVOH, is the heat sealable outer layer, and provides structural stability. [8]

This research will initially determine if the PP is able to retain its properties after the retort process and secondly, if the addition of nanoparticles compounded into the EVOH will improve the barrier and mechanical properties of multilayer PP/EVOH/PP film. Polymer nanocomposites have previously shown a significant improvement in mechanical and barrier properties when compared to neat films. [9] The dispersion of the nanoparticles creates a toturous path which improves the barrier properties of the polymer film.

Experimental

Materials

The EVOH was provided by EVALCA. It is an EVOH E-105 series grade. This series of EVOH is 44mol% ethylene. A decreasing mol% ethylene provides higher barrier properties while an increasing mol% provides tensile strength, flexibility and retortability. The melting point and glass transition temperatures this series are 165°C and 55°C respectively. [10, 11, 12] The retort grade PP was provided by Huntsman. The melting point and glass transition temperatures of PP are 175°C and -18°C respectively. The MLS which was provided by

Southern Clay Products, Cloisite 25A, is montmorillonite clay modified with a quaternary ammonium salt. [13] The material grades are summarized in Table 1.

Processing

Pure PP Control

The PP monolayer cast film was processed using a ThermoHaake PolyLab extruder (RC300P/R600) with a cast film die; the processing conditions are shown in Table 2.

EVOH/MLS Compounding

The EVOH/MLS Cloisite 25A was compounded at Triton Systems, Inc. using a Zenix ZPT-30, 30 millimeter co-rotating twin screw extruder.

Multilayer Film

The multilayer cast film was processed using a Collin Teach-Line Co-Extruder (CR72T) which consists of three extruders, all with a 25:1 L/D ratio and a 20 millimeter screw. The PP/EVOH/PP and PP/EVOH+MLS/PP were both processed using identical processing conditions, shown in Table 3.

Pouch Fabrication and Retort Conditions

The monolayer cast film and the multilayer cast film were measured and cut to produce prototype pouches for subsequent retort processing; the dimensions of the pouches were 19.05 x 6.98 cm. The pouches were filled with distilled water and vacuum sealed to simulate the retortable MRE pouches which are filled with food products and retorted to sterilize the products inside. The retort machine used was the Validator 2000 Vertical Water and Steam Retort, which cooked the pouches for 30 minutes at 121°C.

Characterization

Mechanical Properties

The tensile properties of the monolayer and the multilayer film were tested using an Instron 4400R following ASTM D-882 while the seal strength properties followed ASTM F-88.

Barrier Properties

The OTR of the monolayer and multilayer film was tested using a MOCON Ox-Tran 2/20 following ASTM D-3985, at 0% relative humidity, 100% O_2, and at 23°C. The WVTR of the monolayer and multilayer film was tested using a MOCON Perma-Tran W 3/31 following ASTM F-1249, at 90% relative humidity, and at 37.8°C.

Results and Discussion

Monolayer Films

Retort Effects

The prototype monolayer PP pouch dimensions after the retort test were constant and there was no change in the color or texture of the pouches. The monolayer pouches were exposed to the retort process and the results indicate that this grade of PP can withstand the process without sacrifice in properties.

Mechanical Properties

The tensile properties of the monolayer film before and after retort were tested and compared. Young's modulus increased by 18% and toughness increased by 32% for the cast film samples after retort. The seal strength of the monolayer films was tested before and after retort to determine how the retort process affected the seal strength. However, the change in seal strength was negligible.

Barrier Properties

The OTR and WVTR are critical for product quality and shelf life and are therefore critical for the multilayer film in this experiment. The OTR decreased for the monolayer films after the retort process, as shown in Figure 3; while the WVTR for all the monolayer PP samples increased by 17% after retort.

Multilayer Films

Moisture Analysis

Prior to processing, the pure EVOH and EVOH/MLS materials were dried and their moisture content analyzed using a Mitsubishi Chemical CA-100 Moisture Meter. The moisture content was 0.1528% for the pure EVOH and 0.1568% for the EVOH/MLS.

Retort Effects

Table 3 shows the multilayer PP and EVOH cast film structures. The multilayer PP and EVOH pouches turned from clear to opaque white after the retort process. The film thickness increased by approximately 25 microns after the retort, which is possibly from water uptake of the EVOH. The film thickness measurements are shown in Table 4. The multilayer cast film was evaluated by scanning electron microscopy however it was not possible to distinguish any individual layers.

Mechanical Properties

The modulus decreased for all pure EVOH and EVOH/MLS multilayer samples after retort. The addition of nanoparticles to the EVOH increased Young's modulus of the multilayer film initially; however, the improvement in properties was not retained after the retort process. Figure 1 shows the before and after retort modulus comparison of the multilayer film. Figure 2 shows that the toughness of the pure EVOH multilayer samples increased by 62% after retort; while the toughness of the

EVOH/MLS samples decreased after retort. The toughness of the EVOH/MLS multilayer film was less than the toughness of the pure EVOH multilayer film before and after the retort process. It can be seen that the standard deviation of the PP/EVOH/PP after retort is large, which shows that there was significant variation.

Seal Strength

The seal strength for the multilayer films was approximately 75% lower than the seal strength for the monolayer films, showing that there was not sufficient layer adhesion. The seal strength increased by 18% for the EVOH/MLS films and by 8% for the pure EVOH multilayer films after the retort process. The seal strength for the EVOH/MLS film samples was greater than the pure EVOH film samples both before and after retort. The addition of nanoparticles improved the heat seal strength of the multilayer film before and after retort process. It was noticed that the samples were delaminating during the tensile testing which might have skewed the results. Further

Barrier Properties

It was found that before retort the OTR of the pure EVOH multilayer film was 0.40 cc/ (m^2-day) but the OTR of EVOH/MLS multilayer film was 1.10 cc/ (m^2-day). The WVTR of the EVOH/MLS was 57% lower than the pure EVOH film. Table 4 shows the OTR and WVTR data for the multilayer films. It was unexpected that the pure EVOH samples would have a lower OTR than the EVOH/MLS samples because the nanocomposites are supposed to create a toturous path which the molecules have to follow in order to permeate the material. After the retort the pure EVOH and EVOH/MLS multilayer films were tested with the Ox-Tran five times for consistency and accuracy, but failed the test all five times. A sample failure is when the OTR exceeds the upper limit of the sensor range which is 2000 cc/ (m^2-day), although there is some flexibility for the actual failure value. [14] EVOH is primarily used as an oxygen barrier; since the OTR failed after retort it was not necessary to test the WVTR. The OTR and WVTR of the multilayer films were not found to meet the military specifications. Although the transmission rates did not meet the military food packaging specifications, further experimentation with different materials or a PP nanocomposite outer layer could lead to a structure which meets the required specifications.

Conclusions

This experiment showed that retort PP and EVOH multilayer film with or without nanocomposite particles does not retain its initial mechanical or barrier properties after the retort process. The EVOH/MLS multilayer showed an improvement over the pure EVOH multilayer in some properties such as Young's modulus, seal strength and WVTR before retort; however, the improvement in properties was lost after the retort process. The EVOH lost all of its initial barrier properties after the retort process, with and without nanocomposites. It was found that the addition of nanocomposites to the EVOH in a multilayer PP film structure did not improve the mechanical properties after retort. This research is continuing with PP/MLS as the outer layer to observe any changes in retort properties.

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Keywords

Nanocomposite, polypropylene (PP), ethylene co-vinyl alcohol (EVOH), retort

Table 1. Materials in Multilayer Structure

Polypropylene	Huntsman P4G2Z-159 Retort Grade
Ethylene Co-Vinyl Alcohol	EVALCA E105 series EVOH
Tie Layer	Mitsubishi Chemical Modic-AP
Montmorillonite Layered Silicate (MLS)	Southern Clay Cloisite 25A Nanoparticle

Table 2: Monolayer and Multilayer Film Processing Parameters

		Screw Speed (rpm)	Zone Temperatures (°C)
Monolayer Film	Cast PP	62	190, 210, 230, 240
Multilayer Film	PP	77	185, 190, 200, 220, 240
	EVOH	60	245, 260, 250, 265, 230
	Tie Layer	79	200, 215, 225, 225, 240

Table 3. Multilayer Film Structure

Polypropylene
Tie Layer
Pure EVOH or EVOH/ MLS
Tie Layer
Polypropylene

Table 4. Oxygen and Water Transmission Rates for Multilayer Structures

Sample ID	Average Thickness (mil)	OTR cc/(m^2-day)	Average Thickness (mil)	WVTR g/(m^2-day)
Before Retort				
PP/EVOH/PP	10.59	0.40 ± 0.1040	10.60	0.69 ± 0.14
PP/EVOH+MLS/PP	11.29	1.10 ± 0.0018	11.24	0.44 ± 0.01
After Retort				
PP/EVOH/PP	12.69	FAIL (5x)		
PP/EVOH+MLS/PP	14.13	FAIL (5x)		

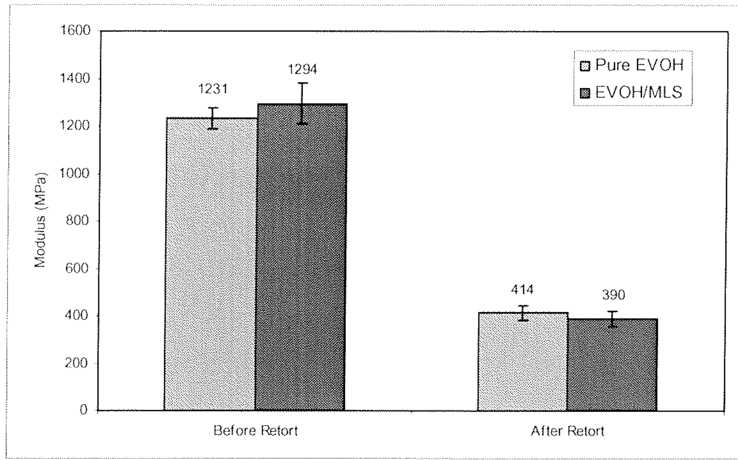

Figure 1. Modulus comparison of multilayer film before and after retort.

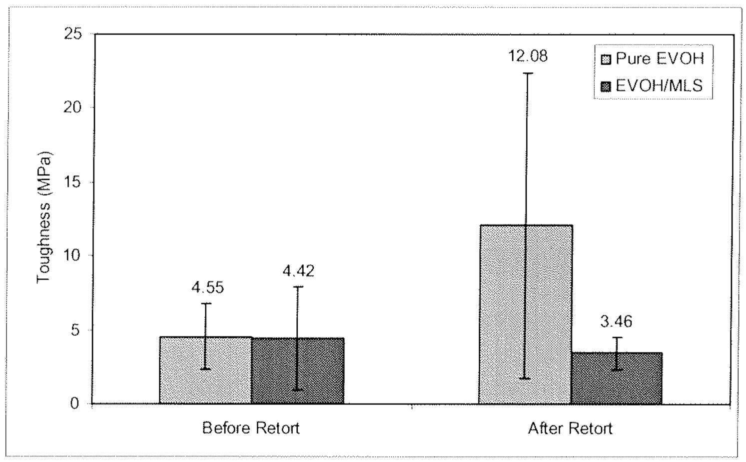

Figure 2. Toughness comparison of multilayer film before and after retort.

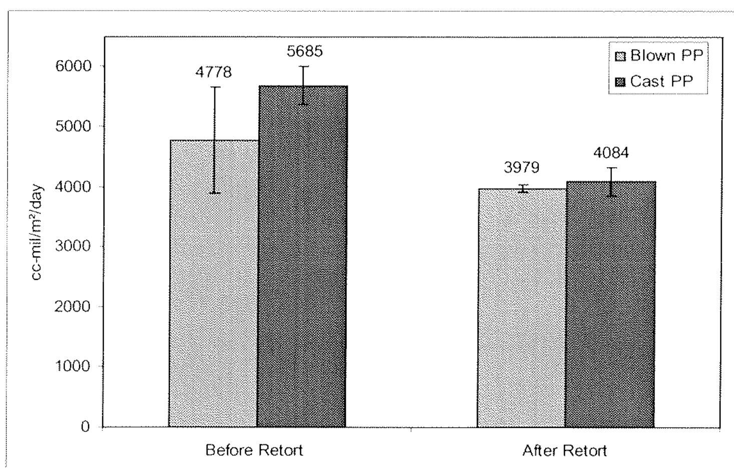

Figure 3. Oxygen transmission rate comparison of cast film before and after retort.