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Comparative Study of Mechanical Properties on LDPE/Clay and LDPE-g-MA/Clay Nancomposites for Film Packaging Applications

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Abstract

The concept of nanoscale reinforcement provides opportunity for synthesis of polymer materials with unique properties. Behavior of LDPE and LDPE-g-MA nanocomposites containing different nanofillers, such as nanoclay (Cloisite®30B) were investigated. Samples were prepared with the nano content 1 to 5 wt % and their mechanical properties such as Tensile Strength, Young's modulus, Impact strength have been considered. Transition Electron Microscopy (TEM) and Wide Angle X-Ray Diffraction (WAXD) were in support of the formation of partially delaminated nanocomposite material.

Keywords: Nanocomposites, LDPE, LDPE-g-MA, Clay, Mechanical Properties.

1. Introduction

In the past three decades, many new polymers have been introduced into packaging markets. These new polymers have provided a unique combination of properties. These polymers provide increased toughness, allowing film manufacturers to produce films at reduced gauges, while maintaining physical properties. High pressure low density polyethylene (LDPE) which have been available for over fifty years, continue to be key players in many produce and food packaging markets, especially those in which high clarity and good sealing characteristics are required. Often, these resins are used for applications because of historical reasons, rather than for a specific property advantage [1].

Over the last two decades, the addition of nano-sized layered silicates in polymers has been found to offer improvements to above-mentioned properties with just a small quantity, typically in the range of 5 wt%. These materials normally called polymer-layered silicates nanocomposites have gained tremendous interest in both the academic and research fields due to their unique structure as well as properties (Dennis et al., 2001) [2].

In this study, PE/clay nanocomposites with compatibilizing agent, PEMA, were investigated in film samples using to twin screw extruder for properties testing. The effect of clay on mechanical and gas barrier properties were considered in the various clay loadings. The orientation of clay platelets and the degree of crystallinity of polymer that affected the mechanical properties of nanocomposites were also discussed.

2. Experimental Materials and Techniques

2.1. Materials

The clay material is Cloisite®30B from Southern clay products. It is a natural montmorillonite organically modified with a methyl tallow bis-2-hydroxyethyl quaternary ammonium. The as-received clay (montmorillonite) particles were disk-like stacks of thin silicate layeres, 1 nm thick and ranging from 100 nm to several micrometers in diameter (with an aspect ratio ranging between 200 and 1000).

Low-density polyethylene (LDPE) is a thermoplastic made from the monomer ethylene. It was the first grade of polyethylene, produced in 1933 by Imperial Chemical Industries (ICI) using a high pressure process via free radical polymerization. Its manufacture employs the same method today. The EPA estimates 5.7% of LDPE (recycling number 4) is recycled. Despite competition from more modern polymers, LDPE continues to be an important plastic grade. LDPE is defined by a density range of 0.910–0.940 g/cm^3. It is not reactive at room temperatures, except by strong oxidizing agents, and some solvents cause swelling. It can withstand temperatures of 80 °C continuously and 95 °C for a short time. Made in translucent or opaque variations, it is quite flexible, and tough but breakable. LDPE has more branching (on about 2% of the carbon atoms) than HDPE, so its intermolecular forces (instantaneous-dipole induced-dipole attraction) are weaker, its tensile strength is lower, and its resilience is higher. Also, since its molecules are less tightly packed and less crystalline because of the side branches, its density is lower. LDPE contains the chemical elements carbon and hydrogen.

Table 1 : Properties of Cloisite®30B.

Property	**Value**
% Moisture	< 2%
Specific Gravity, g/cc	1.98
Loose Bulk, lbs/ft3	14.25
Packed Bulk, lbs/ft3	22.71

Table 2: Physical properties of LDPE.

Property	**Value**
Density	0.92 g/cm³
Surface hardness	SD48
Max. operating temp.	50 °C
Water absorption	0.01%
Oxygen index	17%
Dielectric strength	25 MV/m
HDT @ 0.45 Mpa	45 °C
HDT @ 1.80 Mpa	37 °C
Material drying	NA
Melting Temp. Range	120 to 160 °C
Mould Shrinkage	3%
Mould temp. Range	20 to 60 °C

Glycidyl methacrylate (GMA) is an ester of methacrylic acid and a common monomer used in the creation of epoxy resins. While typical home epoxies contain diglycidyl ether of bisphenol A (DGEBA), glycidyl methacrylate is instead used to provide epoxy functionalization to polyolefins and other acrylate resins. as can be seen in Table 3.

Table 3: properties of GMA.

Property	**Value**
Appearance	Clear, colorless liquid
Boiling Point@ 760 mm Hg	189°C (372.2°F)
Freezing Point	<-70°C (<-94°F)
Density @ 25°C (77°F) @ 66°C (150°F)	1.068 g/ml (8.91 lb/gal) 1.03 g/ml
Refractive Index @ 25°C	1.4473
Solubility	2.3%
Vapor Pressure @ 25°C (77°F) @135°C (275°F)	0.33 mm Hg 112 mm Hg
Viscosity @ 15.5°C (60°F)	2.7 cPs
Molecular Weight	142.15

2.2. Grafting Process

The grafting reaction is carried out in an internal mixer (Rheomix 3000p Haake mixer). LDPE pellets mixed with varying amounts of GMA (5, 10 phr) are fed into the mixer. The processing temperature is 180°C. The speed of rotor is 60 rpm and the mixing time is 10 minutes.

2.3. Sample Preparation

LDPE and PE-g-MA, and Clay melt-mixed by twin-screw (ZPT-32HT) with 160˚C temperatureand. The speed of rotor is 150 rpm for 20 minutes with different weight ratios, as can be seen in Table 4 were prepared.

Table 4 : Nanocomposites Sample with different content.

MMT (wt %)	LDPE (wt %)	LDPE-g-MA (wt %)	Compositon
0	-	100	LDPE
1	-	99	LDPE/MMT-1
2	-	98	LDPE/MMT-2
3	-	97	LDPE/MMT-3
4	-	96	LDPE/MMT-4
5	-	95	LDPE/MMT-5
0	100	-	LDPE-g-MA
1	99	-	LDPE-g-MA/MMT-1
2	98	-	LDPE-g-MA/MMT-2
3	97	-	LDPE-g-MA/MMT-3
4	96	-	LDPE-g-MA/MMT-4
5	95	-	LDPE-g-MA/MMT-5

2.4. Characterization

Most TEM and XRD was done by the member that prepared the sample. TEM analysis can reveal. Low magnification TEM will reveal how well dispersed the clay is throughout the polymer, and it can also show the degree of intercalation and exfoliation which occurred [4].

2.4.1.Wide Angle X-Ray Diffraction

Wide Angle X-Ray Diffraction (WAXDS) were performed on siemence D5000 X-ray diffractometer with Cu radition(wavelength 0.15418 nm) operated at 40 KV and 30 mA. The diffraction curves were collected atscanning rate 0.02°/s and step size of 0.02°.

XRD is a useful screening tool for determining if any sort of nanocomposite was prepared, but the results provided by XRD cannot be used alone to define the exact nature of the nanocomposite. XRD only gives the distance between clay layers, thus revealing the relationship of the clay layers to themselves, not of the clay layers to the polymer. XRD does not reveal how well dispersed the clay is throughout the polymer, nor does it define the degree of intercalation or exfoliation.

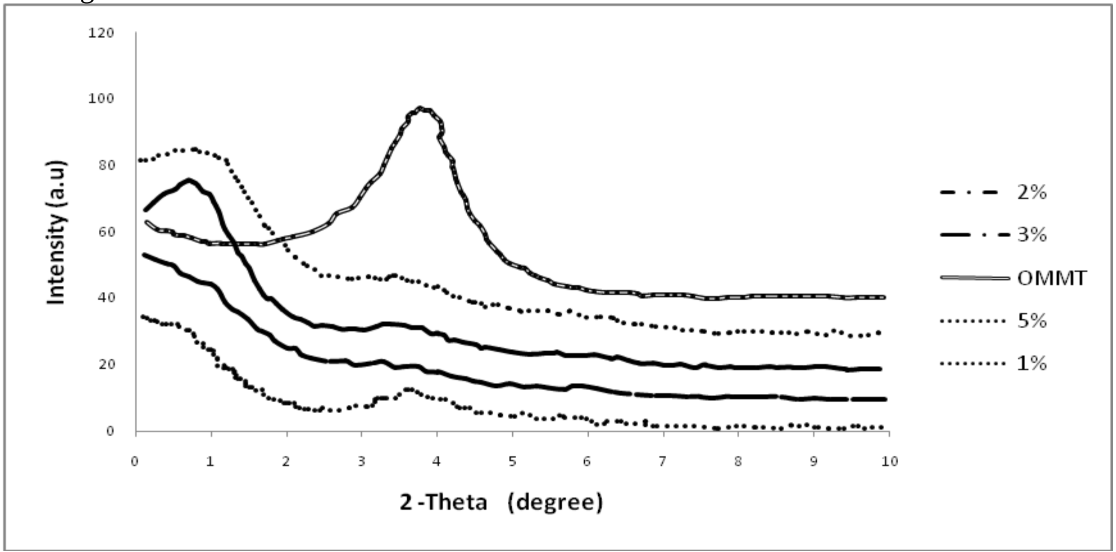

Figure 1: XRD-Spectra for Cloisite®30B (Clay) and LDPE-g-MG nanocomposite with different Clay.

Figure 1 presents the WAXDs of LDPE/Clay nanocomposite as well as clay nanoparticles. Figure 1 do not show any sharp crystalline diffraction peaks in this nanocomposie and we can find clay to disperse in LDPE matrix well.

2.4.2.TEM

TEM samples were prepared using cryo ultramicrotomy (-110 °C) to cut 70 nm thick sections. These sections were placed onto carbon-coated copper grids. Bright-field TEM images were obtained at 120 kV, at low dose conditions, with a Philips 400T at magnifications of 2800, 10000, 28000, and 60000 ×. TEM negatives were then enlarged to 8400, 30000, 280000, and 600000× respectively to produce high magnification prints. The contrast between the layered silicates and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging was required.

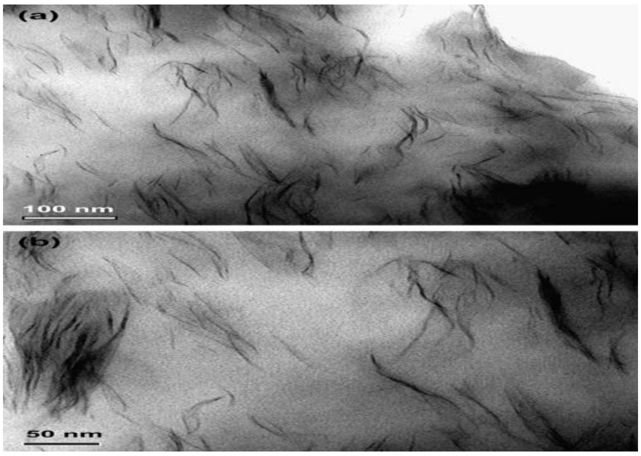

Figure 2: TEM for LDPE-g-MA nanocomposite with 5% clay.

Figure 2 shows the TEM photographs of the emulsion of LDPE-g-MA nanocompoistes (with Clay content of 5 %). The clay was exfoliated into thin layers and well mixed with the LDPE. It can be observed from Figure 2 that Clay has been delaminated into nanoscale layers and is dispersed throughout LDPE matrix.

2.5. Mechanical properties

The bulk properties of a polymer are those most often of end-use interest. These are the properties that dictate how the polymer actually behaves on a macroscopic scale.

2.5.1. Stress-Strain

The mechanical properties was measured for film (50–60 lm in thickness) using INSTRON machine at a cross speed of 50 mm/min. Five specimens were prepared for each sample for MD tests. To compare 5 wt % clay nanocomposite with neat PE, typical stress– strain diagrams are shown in Figures 3, respectively.

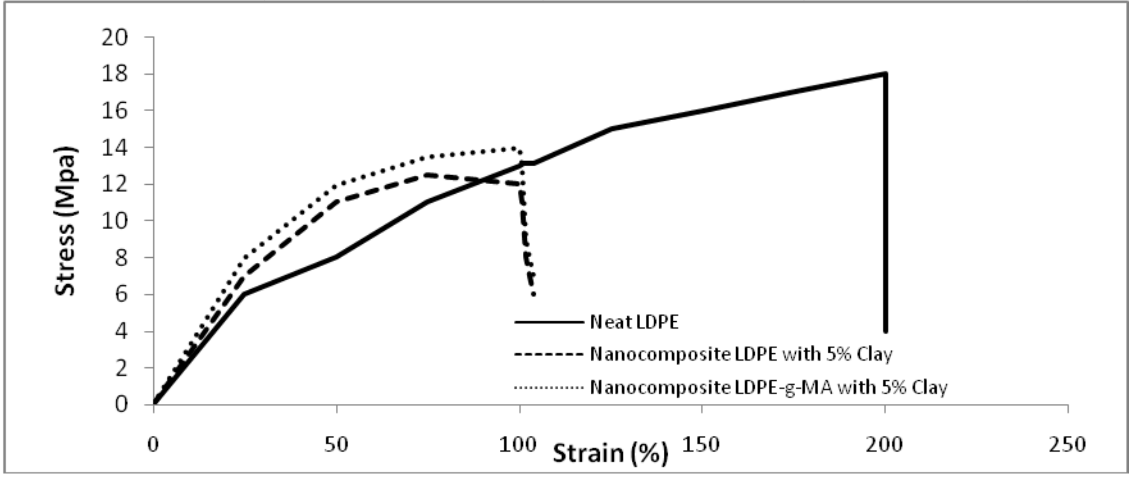

Figure 3: Stress–strain diagrams of neat PE , 5 wt% of clay in PE/clay nanocomposite and 5 wt% of clay in PE-g-MA/clay nanocomposite for MD tests.

2.5.2. Young´s Modulud

Young's Modulus quantifies the elasticity of the polymer. It is defined, for small strains, as the ratio of rate of change of stress to strain. Like tensile strength, this is highly relevant in polymer applications involving the physical properties of polymers, such as rubber bands.

The modulus is strongly dependent on temperature. Viscoelasticity describes a complex time-dependent elastic response, which will exhibit hysteresis in the stress-strain curve when the load is removed.

Young's modulus for nanocomposite samples can be seen in Figure 4. Young's modulus for pure LDPE is 50 Mpa, and Young's modulus increases when clay was added.

The maximum value of the Young's modulus of the Clay/LDPE nanocomposite is 121 Mpa (with Increasing % 51/25 compared to pure LDPE) ,So we can see the maximum value in LDPE-g-MA/Clay nanocomposte (with Increasing % 62/1 compared to pure LDPE-g-MA).

As cab bee seen in Fgure. 4. Young's modulus ratios increased with increasing the clay. As a result , exfoliated LDPE-g- MG/Clay nanocomposites were produced.

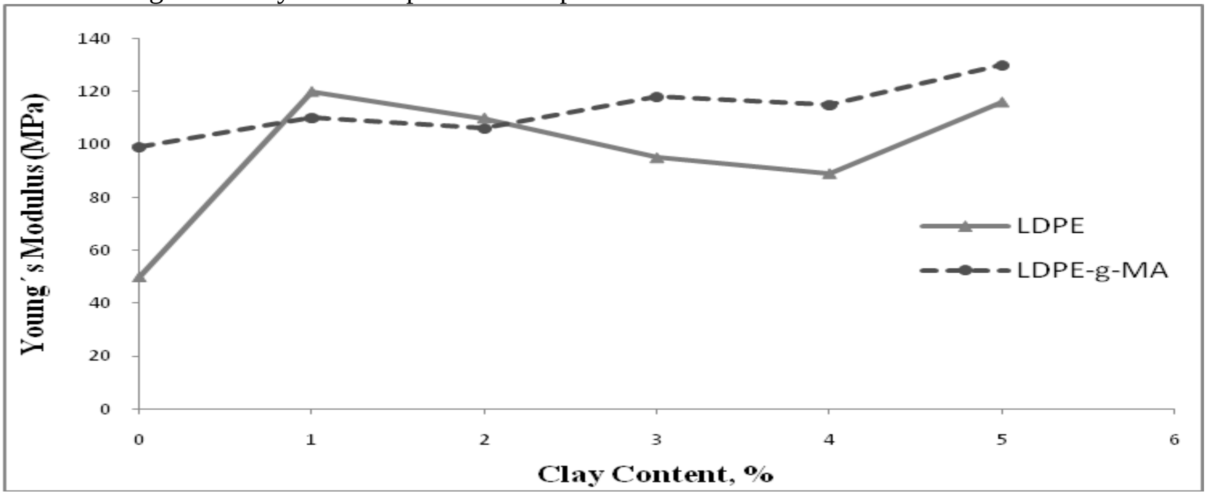

Figure 4: Young's modulus of LDPE and LDPE-g-MA nanocomposites.

2.5.3. Flexural Strength Testing of Plastics

The flexural strength of a material is defined as its ability to resist deformation under load. For materials that deform significantly but do not break, the load at yield, typically measured at 5% deformation/strain of the outer surface, is reported as the flexural strength or flexural yield strength. The test beam is under compressive stress at the concave surface and tensile stress at the convex surface. The figure below, from Quadrant Engineering Plastic Products, shows the test geometry for ASTM D790.

ASTM D790:

Specimen of 1/8" x 1/2" x 5" is placed on two supports and a load is applied at the center. The load at yield is the sample material's flexural Test.

Flexural strength for nanocomposite samples can be seen in Figure. 5.

The minimum value of the flexural strength is on the Clay/LDPE-g-MA nanocomposite with 5% content clay (with Increasing % 8/5 rigidity).

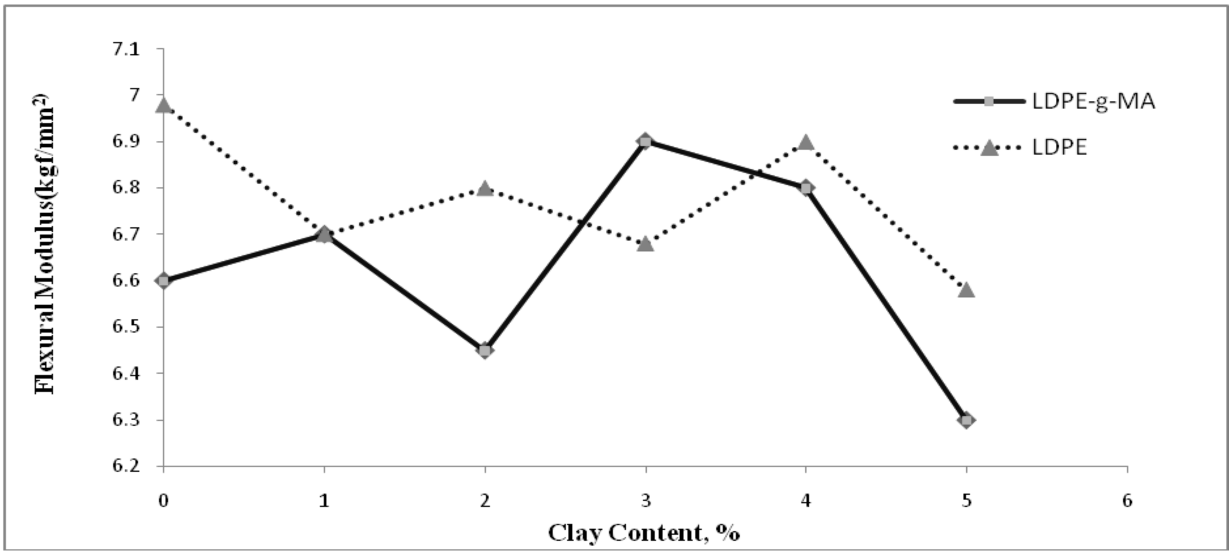

Figure 5: flexural strength of LDPE and LDPE-g-MA nanocomposites.

Conclusions

Exfoliated LDPE nanocomposites were synthesized by using nanofillers while intercalated nanocomposite were obtained with nanofillers.

The morphology and mechanical properties of nanocomposites were investigated with various techniques (Transition Electron Microscopy images of specimens, proper distribution of nanoparticles shows LDPE). Compared with sheet-like nanoclays show some advantages on LDPE some important thermophysical properties.

Final results showed that LDPE-MA-MMT compared to LDPE / MMT and some mechanical properties such as Young's modulus of pure LDPE, with better performance.

Acknowledgements

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