

The Effect of Addition of Dioctyl Terephthalate and Calcite on the Tensile Properties of Organoclay/Linear Low Density Polyethylene Nanocomposites

A. Gürses, Z. Eroğlu, E. Şahin, K. Güneş, Ç. Doğar

Abstract—In recent years, polymer/clay nanocomposites have generated great interest in the polymer industry as a new type of composite material because of their superior properties, which includes high heat deflection temperature, gas barrier performance, dimensional stability, enhanced mechanical properties, optical clarity and flame retardancy when compared with the pure polymer or conventional composites. The investigation of change of the tensile properties of organoclay/linear low density polyethylene (LLDPE) nanocomposites with the use of Dioctyl terephthalate (DOTP) (as plasticizer) and calcite (as filler) has been aimed. The composites and organoclay synthesized were characterized using the techniques such as XRD, HRTEM and FTIR techniques. The spectroscopic results indicate that platelets of organoclay were well dispersed within the polymeric matrix. The tensile properties of the composites were compared considering the stress-strain curve drawn for each composite and pure polymer. It was observed that the composites prepared by adding the plasticizer at different ratios and a certain amount of calcite exhibited different tensile behaviors compared to pure polymer.

Keywords—Linear low density polyethylene, nanocomposite, organoclay, plasticizer.

I. INTRODUCTION

IN recent years, polymer/clay nanocomposites have received an intensive attention with the prominent improvements in their mechanical and thermal properties by the addition of a very few amount of clay compared to conventional composites. These improvements especially depend on the exfoliation or random dispersion degree of clay platelets in the polymer matrix [1]-[3]. Polymer/clay nanocomposites (PNCs) are a new class of composite materials which have attracted much interest in recent years, due to their superior mechanical, thermal and barrier properties compared with virgin polymer or conventional micro-composites [3]-[5]. Currently, the PCN material is found to be a promising system due to the fact that the clay possesses a high aspect ratio and a platy morphology. PNCs can be employed to boost the physical properties of polymers, e.g. thermal stability [6], fire retardant [7], gas barrier [8], and corrosion protection [9], as well to improve the

mechanical properties of polymers [10]. In order to enhance physical and mechanical properties of LLDPE, some additives can be added to it. Fillers and reinforcement used include talc, calcium carbonate (CaCO_3), mica, wollastonite, glass fiber, glass bead, jute, etc. CaCO_3 is one of the most abundant minerals in the earth's crust [11].

Plasticizers are by far the most common additives. They are also less expensive than other additives used in the polymers processing and applications [12]. DOTP, a compound commonly used as plasticizer in plastics, paints and varnishes. Moreover, the fact that the melting and boiling points for DOTP are 225 K and 673 K can provide a wider low temperature working range [13].

The goal of this study is to examine the effect of adding of DOTP (as a plasticizer) and calcite (as filler) onto the tensile properties of organoclay/LLDPE nanocomposites. It will be studied also to elucidate the mechanisms of mutual interaction between plasticizer molecules, the polymer chains and clay plates.

II. MATERIALS AND METHODS

A. Materials Used

For the synthesis of nanocomposites and organoclay, it was used mainly a layered clay, which was Montmorillonite supplied from Çankırı-Turkey, LLDPE and Cetyltrimethylammonium bromide (CTAB). The cation exchange capacity (CEC) of clay was determined to be 147.9 meq/100 g by the methylene blue method (ANSI/ASTM C837-76) [14]. The chemical composition of MMT, which has been determined by X-ray fluorescence spectrometry technique, was given in Table I. The some typically properties of commercial long chained hydrocarbon used in this study have been shown in Table II. All chemicals used in this study were supplied from Merck.

B. Preparation of Organoclay/LLDPE Nanocomposites

Organoclay/LLDPE nanocomposites were prepared by melt intercalation using a single-screw extruder at a temperature range of 190–210 °C and a screw speed of 145 rpm. The addition of DOTP and calcite was made prior to the extrusion. Finally, the strands obtained from the extruder were mechanically pressed.

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TABLE I
THE CHEMICAL COMPOSITION OF THE LAYERED CLAY USED

SiO ₂	59.32
Al ₂ O ₃	17.19
CaO	2.21
MgO	3.63
Fe ₂ O ₃	5.95
K ₂ O	0.97
Na ₂ O	1.68
TiO ₂	0.74
SO ₃	0.51
Other	7.81

TABLE II
SOME PHYSICAL AND CHEMICAL PROPERTIES OF LONG-CHAIN
HYDROCARBON USED IN THIS STUDY

Density (15 °C), kg/m ³	990.7
Calorific value MJ/kg	42.74
Flash point °C	105.8
Water by distillation, wt %	0.1
C	83.4
H	11.9
N	0.8
S	1.5
Ash	0.03

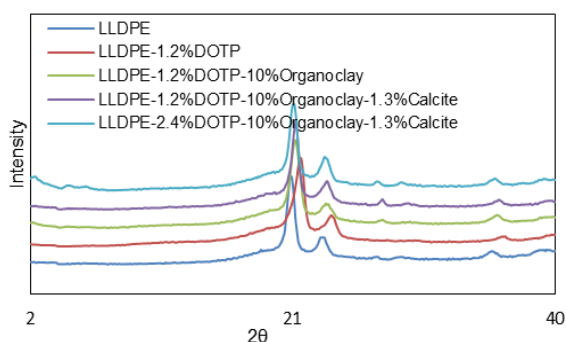


Fig. 1 XRD patterns for the virgin PE and the composites which were prepared using DOTP, clay and calcite

C. Characterizations of Organoclay and Organoclay/LLDPE Nanocomposites

Many techniques, such as XRD, FT-IR, and DSC have been incorporated to characterize the nanocomposites and to evaluate their thermal stabilities in this study. XRD measurements of the organo-clay samples were performed using Rigaku 2200D/max (Rigaku Corporation, Tokyo, Japan) powder diffractometer equipment with a CuK α radiation source. The FTIR spectra for the composites were taken on by using a Perkin-Elmer Spectrum-One and KBr pelleting method for a range of 4000–400 cm⁻¹ at a scanning rate of 2°/min. All measurements were obtained by an average of 100 scans and a resolution of 1 cm⁻¹. In order to estimate the framework rearrangement of nanocomposites, the specimens from the samples were examined by using a JEOL 2100 high resolution transmission electron microscope (HRTEM) (LaB6filament) operated at 200 Kv. The curing behaviors of nanocomposites were observed with a differential scanning

calorimeter (DSC7020) under nitrogen atmosphere. A typical sample weight was about 10 mg and the scan speed was 20 °C/min. Tensile strength measurements were conducted by Shimadzu AG-I universal tensile testing machine at 18 °C and 30% humidity environment at a deformation rate of 1 mm/min.

III. RESULTS AND DISCUSSION

A. XRD Analysis

Fig. 1 shows the XRD patterns of pure LLDPE and the composites, which were prepared using DOTP, organoclay and calcite.

X-Ray Diffraction (XRD) is one of the techniques used to prove the formation of a nanocomposite. With this technique, the intercalation of clay in the polymeric matrix can be determined by comparing the diffraction peak of the modified and unmodified material [15]. From Fig. 1, it can be seen that the organoclay platelets predominantly exfoliated in the polymer matrix. The dispersion of clay particle was not affected markedly by the addition of calcite. This can be attributed to a decrease in the interfacial energy of calcite/polymer chains as a result of the interactions between DOTP molecules and calcite particles.

B. FTIR Analysis

FTIR spectra for pure LLDPE and the composites, which were prepared using DOTP, clay and calcite, were given in Fig. 2.

The stretching peaks that belong to C=O at 1738 cm⁻¹, C-O at 1271.9 and 1116.9 cm⁻¹, alkyl C-H at 2856 and 2940 cm⁻¹ remained at almost the same position for all samples. The peaks at 1577.9, 1504.8 and 1463.4 cm⁻¹ result from the aromatic phenyl ring and the peak at 815 cm⁻¹ is owing to the carbonyl groups of phenyl ring [16], [17].

A significant change observed in the positions of peaks around 2800 cm⁻¹ for two samples containing calcite may be attributed to interactions between the DOTP 'phthalate groups and calcite.

C. DSC Analysis

Differential scanning calorimetric measurements have been widely applied in the investigation of numerous phenomena occurring during the heating of organoclays and PNCs or nanotubes, involving glass transition (T_g), melting, crystallization and curing [18]. The melting point can be determined from the melting curve with pure substances; the melting point corresponds to the onset. Impure samples often show several peaks. The downward movement of the peak in DSC heating curve indicates that the peak is endothermic peak [19]. The DSC spectra of pure LLDPE and the composites were given in Fig. 3.

The DSC results show explicitly that the thermal behavior of the composites was affected to a large extent. In the cases of DOTP, DOTP plus organoclay and DOTP plus organoclay plus calcite, increases in their T_g ranges and melting temperatures were observed. This can be attributed to the fact that the addition of inorganic materials moderates the heat transfer and thus leads to a higher melting temperature [20].

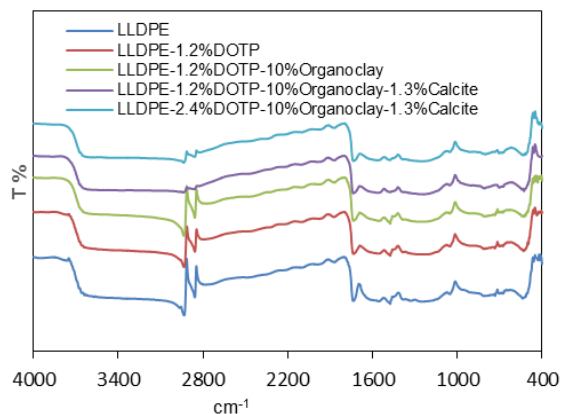


Fig. 2 FTIR spectra of pure LLDPE and the composites which were prepared using DOTP, clay and calcite

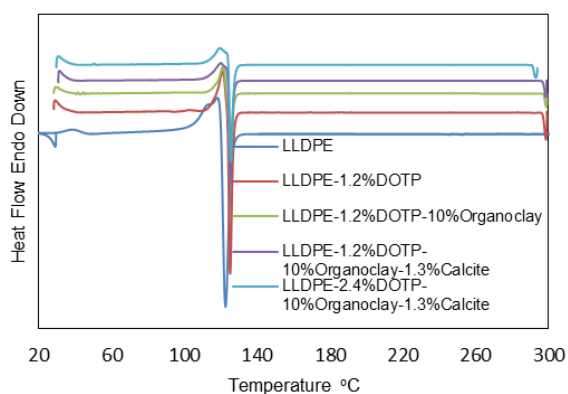


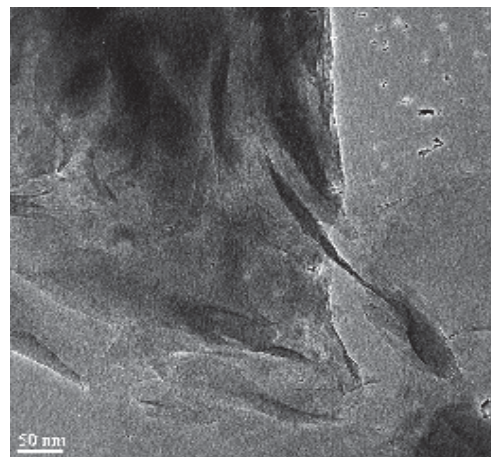
Fig. 3 DSC spectra of pure LLDPE and the composites which were prepared using DOTP, clay and calcite

D. HRTEM Analysis

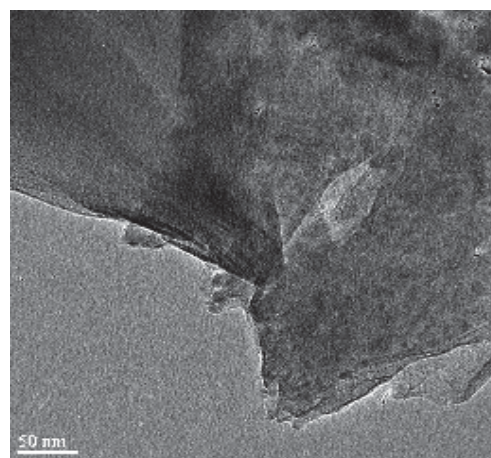
HR-TEM images of raw clay and organoclay were shown in Fig. 4. This figure shows that the organoclay platelets having a high interaction potential with the other components were formed. Thus, it can be suggested that the clay platelets having a high hydrophobicity had the surface characteristics highly compatible with polymer chains and DOTP molecules.

E. Mechanical Analysis

Mechanical properties depend in great measure on the dispersion degree of clay plates [21] and the development of adhesion between clay surface and the polymer chains [22]. Tensile properties of the nanocomposites prepared with different compositions were evaluated in terms of elasticity modules and % elongation reported in Table III. Stress-Strain curves of pure LLDPE and the composites which were prepared using DOTP, clay and calcite were drawn in Fig. 5.



(a)



(b)

Fig. 4 HR-TEM images of raw clay (a) and organoclay (b)

TABLE III
SOME MECHANICAL PROPERTIES OF PURE LLDPE AND THE COMPOSITES
PREPARED BY USING ORGANOCCLAY, DOTP AND CALCITE

	Elasticity Module (MPa)	Elongation (%)
LLDPE	254,60	289,44
LLDPE-1.2%DOTP	251,69	493,69
LLDPE-1.2%DOTP-10%Organoclay	205,48	108,67
LLDPE-1.2% DOTP-10% Organoclay-1.3% Calcite	178,24	661,35
LLDPE-2.4% DOTP-10% Organoclay-1.3% Calcite	227,89	512,68

The addition of DOTP to the polymer caused a serious increase of its elongation percent, while reducing slightly the elasticity modulus of polymer. The increase in the tensile strength may be attributed to effective interactions between the DOTP molecules and polymer chains. However, as can be seen in Table III, by the simultaneous use of DOTP and organoclay, the percent elongation of polymer has significantly decreased, in contrast to polymers containing polar groups, such as PVC [23], [24]. Thus, it can be claimed that the exfoliated clay layers created a disadvantage for the

dispersion of DOTP molecules having a certain charge density. An extraordinary increase observed in the tensile values of two samples containing calcite may be attributed to interactions between the DOTP's phthalates groups and calcite. The measurement results also show that the composite prepared using calcite with DOTP possess the highest stiffness and strength values with respect to the other composites.

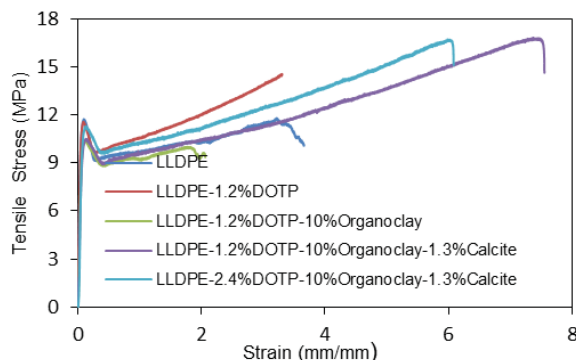


Fig. 5 Stress-Strain curves of pure LLDPE and the composites which were prepared using DOTP, clay and calcite

IV. CONCLUSION

The outstanding results of this study can be summarized as:

- The LLDPE/organoclay nanocomposites which contain DOTP or calcite or both of them were prepared using the melt intercalation method.
- The thermal behaviors of the all composites demonstrate significant changes in terms of their glass transition temperatures and melting temperatures, by addition of DOTP, organoclay and calcite. These changes can be attributed to the possible changes occurring in the crystal structure of the polymer, depending on the type and amount of additives added into the polymer matrix.
- The highest toughness and strength values have been achieved for the composites prepared using plasticizer (DOTP) with calcite.

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