

Flame-Retardant Synergism of Sepiolite and Magnesium Hydroxide in a Linear Low-Density Polyethylene Composite

Rahmat Gul, Atif Islam, Tariq Yasin, Sadullah Mir

Department of Chemical and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, Nilore, P.O. Box 45650, Islamabad, Pakistan

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ABSTRACT: A synergistic effect on flame retardancy, thermal stability, and mechanical properties was found when sepiolite was incorporated into a linear low-density polyethylene (LLDPE)/magnesium hydroxide (MH) composite. Different amounts of sepiolite (up to a maximum concentration of 15 phr) were added to a standard LLDPE/MH formulation, and vinyltriethoxysilane was used as a compatibilizer as well as a crosslinking agent. The thermal stability and the oxidation induction time increased with increasing sepiolite content in the LLDPE composites. Limiting oxygen index (LOI) results indicated an increase in LOI with the addition of sepiolite, and an

LOI value of 36.5% was observed with 15 phr sepiolite in the LLDPE/MH formulation. The addition of sepiolite increased the gel content and tensile strength of all samples and lowered the elongation at break. The heat deflection, Vicat softening temperature, and hardness were also improved by the incorporation of sepiolite. This synergistic behavior of sepiolite with MH could be used in halogen-free, flame-retardant LLDPE formulations. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2772–2777, 2011

Key words: crosslinking; flame retardance; polyolefins

INTRODUCTION

The flammability of polyolefin-based polymers and their melt dripping limit their deployment in many applications such as wires and cables, electronics, and construction. Therefore, improvements in the mechanical properties and flame retardancy of these polymers have become an important subject.^{1,2} Linear low-density polyethylene (LLDPE), a polyolefin-based thermoplastic, has been used in the production of engineering plastics, wires and cables, packaging films, fibers, and so forth. Crosslinking is an effective way of enhancing the mechanical and thermal properties of LLDPE and is broadly used for the modification of polymer properties. Silane, peroxide, and radiation are used to form three-dimensional structures.³ Silane crosslinking is a cost-effective and easy method, and silane-crosslinked LLDPE is used to produce cable insulation. Ultsch and Fritz⁴ studied the silane crosslinking behavior of three different polyethylenes: LLDPE, very low density polyethylene (VLDPE), and a low-density polyethylene (LDPE)/LLDPE blend. The results showed that the structural parameters of polyethylene

strongly affect the grafting and crosslinking performance in the order of LLDPE > LDPE > VLDPE. Silane crosslinking enhances thermal stability; however, silane-crosslinked LLDPE is still combustible, and increased flame retardancy is strongly required.

The wire and cable industry is still using poly(vinyl chloride) and halogen-containing flame-retardant polyolefins as insulation materials. The inherent toxicity of halogenated flame-retardant additives and their persistence in the environment are major environmental concerns. Furthermore, during incineration processes, bromine- and chlorine-containing products are believed to contribute to highly toxic dioxin emissions, and this has led to an increasing demand for low-smoke, zero-halogen flame-retardant additives.^{5,6} Halogen-free flame retardancy is commonly achieved by the incorporation of inorganic fillers [typically magnesium hydroxide (MH) or aluminum hydroxide (ATH)] into the polymer resin. During combustion, metallic hydroxides decompose, release a significant amount of water, absorb heat, and generate a metal oxide coating that can act as an insulating protective layer.^{7–10} The decomposition reaction of MH can be described as follows:



where the change in enthalpy is 1300 kJ/kg. The high decomposition temperature (300–320°C) of MH

Correspondence to: T. Yasin (yasintariq@yahoo.com).

allows it to be used in polymers such as polyethylene and polypropylene for which ATH is not recommended because of its low decomposition temperature (200°C).¹¹ However, the use of MH as a flame-retardant additive in polymers is limited by its low flame retardancy and the large amounts required, which degrade the mechanical properties of polymeric materials.^{12–15} Studies have shown that an MH loading greater than 60% is required to obtain an adequate level of flame retardancy. Therefore, it is necessary to lower the amount by modification and/or mixing with other additives (especially those with a synergism with MH).^{16–19} Significant improvements in flammability and combustion parameters were observed when MH and different types of clays were used.²⁰

Sepiolite has a chainlike structure with the chemical formula $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4\cdot 8\text{H}_2\text{O}$, and it has been used for the preparation of polymer composites.^{21,22} The structure of sepiolite is quite similar to the structure of MH, and it also contains water of hydration and can be used with MH. Recently, sepiolite showed synergistic flame-retardant effects with MH in an ethylene vinyl acetate matrix.²² Here we studied the combined effect of sepiolite and MH in an LLDPE matrix. Vinyltriethoxysilane (VTES) was used as a compatibilizer as well as a crosslinking agent. This synergist behavior of sepiolite with MH in an LLDPE matrix can be used in halogen-free flame-retardant applications.

EXPERIMENTAL

Materials

LLDPE (LL6201; density = 0.926 g/cm³, melt flow index = 50 g/10 min) was supplied by Exxon Mobil Chemical (Riyadh, Saudi Arabia). Dicumyl peroxide (DCP; Sigma–Aldrich Chemie, Germany) was recrystallized with anhydrous methanol. Dibutyl tin dilaurate (DBTDL), VTES, MH with a median particle size of approximately 2 µm, and stearic acid were supplied by Sigma Aldrich Chemie, Steinheim, Germany. Sepiolite was acquired from Australia. Irganox 1010 was obtained from Ciba Speciality Chemical, Basel, Switzerland.

Composite preparation

Samples were prepared by a two-step method that included grafting and crosslinking processes. DCP was dissolved in acetone and mixed with LLDPE; then, it was left for an hour so that the acetone could evaporate. Later, MH, sepiolite, VTES, and stearic acid were mixed thoroughly. A Thermo Haake Poly-Lab Rheomix Internal Mixer, Karlsruhe, Germany with roller rotors was used to mix the additives at

TABLE I
Identification and Formulations of All Prepared Samples

Sample	LLDPE (phr)	DCP (phr)	MH (phr)	Sepiolite (phr)	VTES (phr)
LL ₀	100	0.3	60	0	3
LL ₅	100	0.3	60	5	3
LL ₁₀	100	0.3	60	10	3
LL ₁₅	100	0.3	60	15	3

The concentrations were as follows: 0.05 phr DBTDL, 0.20 phr Irganox 1010, and 1 phr stearic acid.

130°C for 3 min. DBTDL and Irganox 1010 were added to the melted materials, and the temperature was raised to 170°C for another 17 min. The rotor speed was kept constant at 60 rpm. All the grafted samples were heat-pressed at 150°C into sheets (1 and 3 mm) at 200 bars. The sheets were crosslinked by immersion into hot water in a temperature-controlled water bath at 90 ± 1°C for 8 h. The standard formulation of crosslinked LLDPE/MH was selected on the basis of published results.¹⁷ The identification and formulations of all the samples are listed in Table I.

Characterization of the composites

The structural analysis of the composites was performed with Fourier transform infrared (FTIR) spectroscopy. The IR spectra of the films were obtained with an FTIR spectrophotometer (Nicolet 6700, Thermo Electron Corp. Waltham, Massachusetts, USA) by the attenuated total reflection technique with a diamond crystal. The samples were scanned from 4000 to 500 cm^{−1} at a resolution of 6 cm^{−1}, and 132 scans were recorded on average.

The thermal behavior of the composites was studied with a Mettler-Toledo, TGA/SDTA851 instruments, Schwerzenbach, Switzerland under a nitrogen flow (50 mL/min). Each sample (6–8 mg) was heated at a heating rate of 20°C/min from room temperature to a maximum temperature of 800°C.

A differential scanning calorimeter (model Q100, TA Instruments, New Castle, DE, USA) was used to measure the melting temperature (T_m) and oxidation induction time (OIT) of the composites according to a standard method (ISO 11357-6 : 2002). First, each sample was held at 50°C for 5 min under a nitrogen flow of 50 mL/min. The sample was then heated from 50 to 190°C at a heating rate of 10°C/min and held there for 5 min for equilibration still under a nitrogen flow of 50 mL/min. After that, the gas was switched to oxygen with a flow rate of 50 mL/min. The oxidation of the sample was observed as a sharp increase in the heat flow due to the exothermic nature of the oxidation reaction.

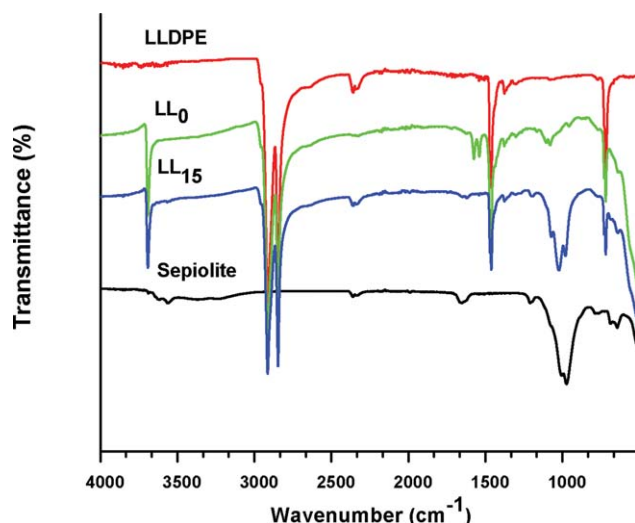


Figure 1 FTIR spectra of LLDPE, sepiolite, LL₀, and LL₁₅ in the mid-IR region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanical tests were performed on a tensile testing machine (model BSS-500kg, SANS, Transcell Technology, Inc., Buffalo Grove, IL, USA) at a cross-head speed of 5 mm/min. Tensile samples were tested according to ASTM D 638, and six specimens were tested for each formulation. All the mechanical properties were performed at room temperature.

The limiting oxygen index (LOI) is a parameter for finding the flame retardancy of polymeric materials in a simulated environment. It denotes the lowest concentration of oxygen (by volume) sustaining candlelike burning of materials in a mixture of nitrogen and oxygen. LOI was measured on an LOI analysis instrument (Dynisco, Heilbronn, Germany) at room temperature. The LOI measurements were carried out in accordance with ASTM D 2863. The dimensions of the specimens used for the test were $100 \times 6.5 \times 3 \text{ mm}^3$.

The gel contents of the crosslinked samples were determined according to ASTM 2765. The samples were cut into small pieces and were placed in a stainless steel mesh and weighed. Extraction with *p*-xylene was carried out for 8 h in a Soxhlet extractor. The extracted specimens were washed with acetone and then dried to a constant weight *in vacuo*. The gel contents of the specimens were calculated with the following equation:

$$\text{Gel content(\%)} = \frac{\text{Weight after extraction}}{\text{Weight before extraction} - \text{Weight of MH+sepiolite}} \times 100$$

The heat deflection temperature (HDT) and the Vicat softening temperature were measured with a Ceast HDT Junior Instrument, Torino, Italy; the tem-

perature was raised at 50°C/h. The dimensions of the specimens agreed with ISO-306 ($80 \times 10 \times 4 \text{ mm}^3$). The HDT was measured under a load of 1.8 MPa, and the Vicat softening temperature was measured under a load of 5 kg.

The hardness was measured with a Reed Model TH210 Shore D Hardness Tester, Houston, USA in accordance with ASTM D 2240. The hardness value was determined by the penetration of the durometer indenter foot into the sample, and averages of 10 readings were recorded.

RESULTS AND DISCUSSION

Structural analysis

Figure 1 shows the IR spectra of LLDPE, sepiolite, LL₀, and LL₁₅. The spectrum of LL₁₅ confirms the presence of sepiolite, MH, and silane in the composite. The peak at 3690 cm^{-1} is due to the O—H band stretching vibration of sepiolite and MH. The peak at 1662 cm^{-1} is attributable to the bending vibration of water. The absorption peaks at 1020 and 1080 cm^{-1} confirm the presence of a siloxane linkage resulting from —Si—O—Si and —Si—O—C, respectively.

Thermal stability

Figure 2 shows the thermograms of LLDPE and other composites, whereas Table II lists the thermal degradation temperatures at various weight-loss percentages as well as the residue percentages at the end of the experiment. Figure 2 shows that the addition of flame-retardant additives improved the thermal stability of the composites. The thermal stability

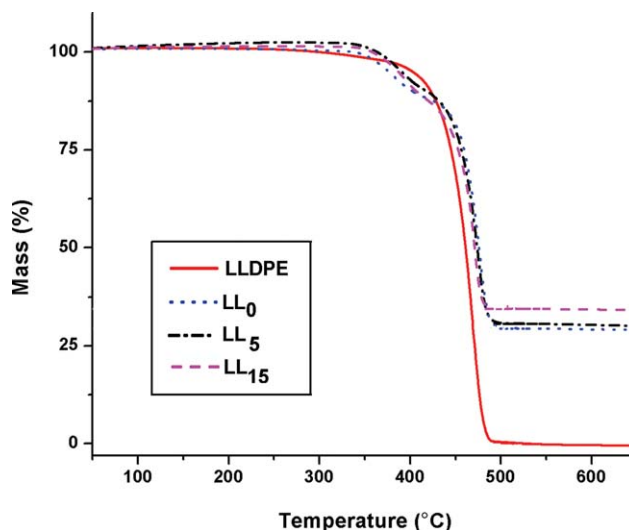


Figure 2 Thermogravimetric analysis profiles of LLDPE, LL₀, LL₅, and LL₁₅ in nitrogen at a heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Thermogravimetric Analysis of the Prepared Samples
at Different Mass Losses

Sample	$T_{10\%}$ (°C)	$T_{25\%}$ (°C)	$T_{50\%}$ (°C)	T_{\max} (°C)	Residue (%)
LLDPE	422.1	445.6	461.4	466.6	0.9
LL ₀	429.7	458.2	475.0	471.6	29.5
LL ₅	434.3	463.7	479.6	474.2	30.1
LL ₁₀	438.8	468.2	482.2	479.1	32.8
LL ₁₅	443.3	472.8	486.4	481.9	34.0

$T_{10\%}$, 10% decomposition temperature; $T_{25\%}$, 25% decomposition temperature; $T_{50\%}$, 50% decomposition temperature; T_{\max} , temperature of maximum decomposition rate.

increased with the concentration of sepiolite increasing. This increase in the thermal stability might be due to the condensation reactions between the —OH group of sepiolite and the silanol groups of VTES, which resulted in a crosslinked product. The addition of sepiolite decreased the onset of thermal degradation for LL₅, LL₁₀, and LL₁₅. The temperature of 10% weight loss for LLDPE was 422.1°C, whereas that for LL₁₅, which contained 15 phr sepiolite, was 443.3°C. An improvement of 21.3°C was observed in comparison with LLDPE. The virgin LLDPE degraded completely at 466°C without any residue, whereas for LL₁₅, the degradation of the polymer resin was completed at 481.9°C with 34% residue.

Differential temperature curves are shown in Figure 3. This figure displays two endothermic responses for the composite formulation. The first endotherm at 340°C shows the decomposition reaction; that is, the removal of water started from MH and sepiolite. The second endotherm around 470°C corresponds to the decomposition of the polymer matrix.

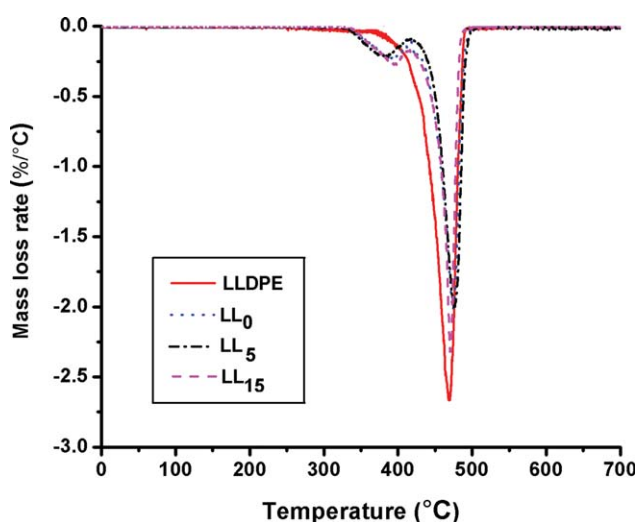


Figure 3 Differential thermogravimetry profiles of LLDPE, LL₀, LL₅, and LL₁₅ under nitrogen at a heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

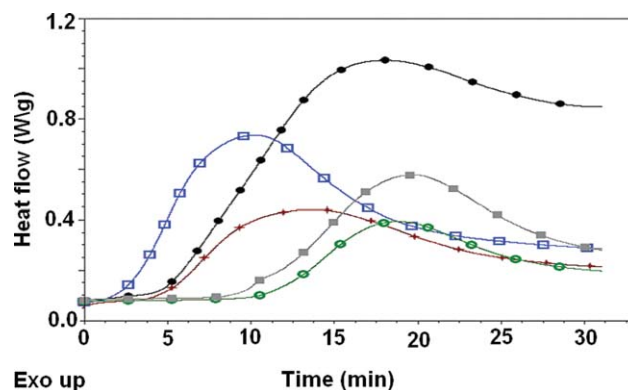


Figure 4 OIT curves for (●) LLDPE, (□) LL₀, (*) LL₅, (○) LL₁₀, and (■) LL₁₅ at 190°C in oxygen (50 mL/min) at a rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

OIT

OIT is used to check the efficiency of additives in polymer materials. A higher OIT value shows that a sample is more resistant to oxidative degradation. Figure 4 shows the OIT curves of LLDPE, LL₀, LL₅, LL₁₀, and LL₁₅. The OIT values are listed in Table III. t_1 is the time at which the atmosphere is changed from nitrogen to oxygen, and t_2 is the time at which an exothermal signal (oxidation) is observed. The OIT value can be determined as the time between t_1 and t_2 .

The OIT value for LL₀ was 2.35 min, and when sepiolite was incorporated into the composite, the OIT value increased to 3.73 min for LL₅. For LL₁₀ and LL₁₅, the OIT values were 8.59 and 9.81 min, respectively. This shows that sepiolite improved the oxidative stability when it was incorporated into the LLDPE/MH formulation. Table III shows the T_m values of the composites. T_m of LL₀ was 125.7°C, and it increased with increasing sepiolite content in the composite. An increase of 2.8°C in T_m was observed with the incorporation of 15 phr sepiolite into the LLDPE/MH formulation.

Mechanical properties

Generally, the addition of a flame retardant causes a decrease in the mechanical properties.^{19,23} Mechanical properties such as the tensile strength and

TABLE III
OIT and T_m Values of the Prepared Samples

Sample	OIT (min)	T_m (°C)
LLDPE	5.00	123.5
LL ₀	2.35	125.7
LL ₅	3.73	126.4
LL ₁₀	8.59	128.1
LL ₁₅	9.81	128.5

TABLE IV
Mechanical Properties of the Prepared Samples

Sample	Tensile strength (MPa)	Elongation at break (%)
LLDPE	10.1 ± 1.8	111.6 ± 1.2
LL ₀	11.9 ± 1.0	1.6 ± 0.3
LL ₅	12.1 ± 0.3	1.4 ± 0.9
LL ₁₀	10.8 ± 0.9	1.3 ± 1.2

elongation at break of the composites have been investigated, and the results are presented in Table IV. Increasing the amount of sepiolite in all cases caused an increase in the tensile strength of the composites, except for LL₁₀. The LL₁₅ sheets became brittle, and it was difficult to cut the specimen.

The elongation at break of the composite samples decreased with the addition of MH and sepiolite to the matrix. For LLDPE, the elongation at break was 111.6%, and the addition of MH to LL₀ drastically decreased it to only 1.6%. The further addition of sepiolite to the LLDPE/MH composite had a negligible effect. This decrease was due to the presence of a large quantity of additives that caused the matrix to lose its ability to withstand elastic deformation. Hence, the composite broke at a lower elastic deformation. The decrease in the elongation at break could also be attributed to the immobilization of the macromolecular chains by the fillers, which limited their ability to adapt to the deformation and made the materials more brittle.²⁴

Flame retardancy

The LOI value is used to measure the flame retardancy of polymers. Table V presents LOI data for LLDPE and its composites. The LOI value of LLDPE was 17.8%, and it increased to 26.0% for LL₀ when 60 phr MH was incorporated into LLDPE. Extensive bubbling was observed during the burning of LLDPE, with the samples rolling over and dripping from the top with large amounts of smoke. LL₀ samples rolled over with a small flame. No dripping and negligible smoke were observed.

TABLE V
LOI Values and Burning Behavior of the Composites

Sample	LOI (%)	Burning behavior
LLDPE	17.8 ± 0.5	The sample rolled over and dripped with large amounts of smoke, and there was extensive bubbling with a liquidlike appearance.
LL ₀	26.0 ± 0.5	The sample rolled over, there was a small flame with minor smoke density, and there was minor bubbling with a solid appearance.
LL ₅	29.4 ± 0.3	The sample kept its standing position with no dripping and negligible smoke, and there was minor bubbling with a solid appearance.
LL ₁₀	34.6 ± 0.7	The sample kept its standing position with no dripping and negligible smoke, and there was minor bubbling with a solid appearance.
LL ₁₅	36.5 ± 0.5	The sample kept its standing position with no dripping and negligible smoke, and there was minor bubbling with a solid appearance.

TABLE VI
Gel Contents, HDTs, Vicat Temperatures, and Hardness Values of the Samples

Sample	Gel content (%)	HDT (°C)	Vicat temperature (°C)	Shore D hardness
LLDPE	—	40.6 ± 0.1	36.6	50.7 ± 0.5
LL ₀	37.6	41.2 ± 0.1	47.9	50.9 ± 0.5
LL ₅	38.4	41.3 ± 0.1	54.1	53.2 ± 0.7
LL ₁₀	43.4	41.4 ± 0.2	57.3	57.0 ± 0.5
LL ₁₅	48.8	45.9 ± 0.1	59.6	57.8 ± 0.6

The addition of sepiolite to the composites further improved LOI and had a synergistic effect on LOI. For LL₅, the LOI value was 29.4%, whereas for LL₁₀ and LL₁₅, the LOI value reached 34.6 and 36.5%, respectively. This showed that a higher oxygen density was needed to initiate the burning of the sepiolite-containing samples and to sustain the smooth combustion of the samples. Moreover, the samples retained their standing position, and no dripping from the top was observed with negligible smoke density. This improvement in LOI showed that during the burning process, sepiolite released its water of hydration, and its endothermic decomposition also absorbed heat from the substrate. The evolution of water vapor and the decomposition products diluted the oxygen in the surrounding atmosphere and improved the LOI value. A similar improvement in the LOI value of ethylene vinyl acetate from 17.8 to 33.0% was observed when a combination of sepiolite (5%) and MH (50%) was used.²²

Gel content

The gel contents of the crosslinked samples are shown in Table VI. The lowest gel content of 37.6% was observed for LL₀, and the gel content increased to 38.4% (for LL₅) when 5 phr sepiolite was added to LL₀. The further addition of sepiolite increased the gel content, and the maximum gel content of 48.8% was observed for LL₁₅. The trend of increasing

gel content with an increasing amount of sepiolite was associated with the possible crosslinking reaction of silanol groups of VTES with hydroxyl groups of sepiolite.

HDT and Vicat softening temperature

HDT is the temperature at which a plastic sample deforms under a specified load. HDT gives the upper boundary of the dimensional stability of a plastic material under a normal load and thermal effects.²⁵ The HDTs and Vicat softening temperatures of LLDPE and other samples are summarized in Table VI. The HDT value of the composite increased with the sepiolite content. The HDT value of LLDPE was 40.6°C, and it increased to 45.9°C for LL₁₅.

The Vicat softening temperature reflects the point of softening to be expected when a material is used in an elevated-temperature application. The Vicat temperature of LLDPE was 36.6°C. For LL₀, the Vicat temperature increased to 47.9°C. The addition of sepiolite had a positive effect on the Vicat temperature, and it increased to 54.1°C in LL₅. A further increase in the sepiolite concentration raised the Vicat temperature to 57.3°C for LL₁₀, and its maximum value of 59.6°C was observed for LL₁₅. The reason for this increase in the Vicat temperature with an increase in the sepiolite concentration might be the increase in the extent of crosslinking, as previously discussed. The addition of sepiolite enhanced the degree of crosslinking, and as a result, the Vicat temperature increased.

Shore hardness

Table VI shows the shore D hardness of LLDPE and its composites. The hardness increased with increases in the sepiolite content of the samples. For the LLDPE sample, the hardness was 50.7, whereas for LL₁₅, its value reached 57.8. This means that the addition of sepiolite increased the hardness of the composites as observed in LL₅, LL₁₀, and LL₁₅.

CONCLUSIONS

Composites of LLDPE with MH and different amounts of sepiolite were prepared. In all formulations, the functionalization of LLDPE was performed by the grafting of vinyl triethoxysilane with DCP as an initiator in a melting process. The crosslinking of additives was carried out in boiling water. Absorption peaks at 1020 and 1080 cm⁻¹ confirmed the presence of siloxane linkages. Thermogravimetric analysis showed that the thermal stability and the amount of the residue increased with an increasing concentration of sepiolite. T_m of LLDPE/MH was

125.7°C, and it increased to 128.5°C with a sepiolite concentration of 15 phr in the formulation. Similarly, OIT values also increased with the addition of sepiolite, and this showed that sepiolite had also improved the oxidative stability of the composites. The LOI value of LLDPE (17.8%) improved and increased to 26.0% in the LL₀ formulation. The addition of sepiolite gradually increased the LOI value, and its maximum value of 36.5% was observed for LL₁₅, which showed synergism between sepiolite and MH. The addition of sepiolite increased the tensile strength of all the samples and lowered the elongation at break. The heat deflection, Vicat softening temperature, and hardness were also improved by the incorporation of sepiolite.

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