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The Effects of Intumescent Flame Retardant and Nanoclay on Mechanical and Thermal Expansion Properties of High Density Polyethylene Composites

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In this work, ammonium polyphosphate and melamine were added as a flame retardant to the nanoclay reinforced high-density polyethylene composites. Ammonium polyphosphate and melamine were added at weight ratios of 0 wt% and 20 wt% to the polymer matrix and their proportions are changed. The addition of nanoclay was carried out at weight ratios of 2 wt% to the polymer matrix. Blending operations were performed by premixing with a mechanical stirrer and melt extrusion technique with twin screw extrusion, respectively. The samples were produced by injection molding. Tensile tests, three-point bend tests, tear tests, the Izod impact tests, and thermomechanical analysis were carried out to investigate the mechanical and thermal expansion properties. Mechanical and thermomechanical test results showed that addition of intumescent flame retardant systems and nanoclay decrease the tensile strength and coefficient of linear thermal expansion values while increasing flexural strengths slightly. However, it has been observed that the addition of additives increases the flexural modulus and density of the polymer composites.

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PACS/topics: high density polyethylene, tensile strength, flexural strength, tear strength, impact resistance, coefficient of linear thermal expansion

1. Introduction

Chemical resistance, good mechanical properties at low-temperatures and low-cost properties makes the high density polyethylene (HDPE) widely useful. Mass production in many cases can be possible with injection, extrusion, and blow molding production techniques. HDPE is petroleum based and therefore, its resistance to heat and fire is low. Different rates of fire retardants have been added to improve these properties, as can be seen in literature [1–6]. Besides, different filler materials can be used to reduce the production costs [1, 2]. Moreover, additives and fillers affect the mechanical and thermal properties of polymers [1–4]. Intumescent flame-retardant systems are used more and more as they do not contain halogens. Xu and his co-authors [5] added ammonium polyphosphate (APP), melamine (MEL), and packaging material powder as intumescent flame-retardant systems to HDPE polymer. They found synergistic effect between APP and MEL reinforced burned layer, which it helps to prevent contact with oxygen. Innumerable flame retardant and filler materials have reduced tensile strength while V0 limits have been reached in UL94 tests. They observed that increasing amount of APP and MEL show crucial degree of flammability besides increased LOI values [5]. Different amounts of nanoparticles and inorganic materials were added to improve the mechanical properties [7–11]. Deka and Maji found that addition of nanoclay (NC) and increasing amount of TiO_2 cause considerable improvement in mechanical properties of HDPE [2]. The addition of NC and fire-retardant materials increase the hardness noticeably [2, 8] despite decrease in the Izod impact strength and coefficient of linear thermal expansion (CLTE) [1, 3, 12, 13].

In this study APP, MEL, and NC additions were made at different ratios to HDPE matrix. The aim of this study is to determine the changes in mechanical and thermal expansion properties of those mentioned composites. Tensile tests, flexural tests, Izod impact tests, hardness tests, and thermal expansion analyses were performed to obtain the mechanical and thermal expansion properties of composites and effects of each additions were compared.

2. Experimental procedure

2.1. Materials

HDPE granules, supplied by Petkim Inc. (İzmir, Turkey), are suitable for injection molding. Petilen I 668 commercial product, with a melt flow rate 5.5 g/10 min (190 °C/2.16 kg) was used as polymer matrix. The intumescent flame retardant system includes APP and MEL. Exolit AP 423 commercial product as APP (the crystal modification is phase II, polymerization degree $>$ 1000) were kindly supplied by Clariant Plastics & Coatings Industry and Trade Inc. (Kocaeli, Turkey). DSM Melamine commercial product was used as MEL which was supplied by DSM Corp. (Heerlen, Netherlands). NC, used as a filler, and containing mass of 6.13% Fe_2O_3, 20.67% Al_2O_3, 53.28% SiO_2, 2.82% MgO, 1.71% CaO,

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0.02% Na_2O, 0.82% K_2O, 0.63% TiO_2, was obtained from Nanokil Ltd. Co. (Erzurum, Turkey). The HDPE granules were coated with polydimethylsiloxane (PDMS) fluid, supplied by Siltech Co. (Toronto, Canada), before extrusion process to spread APP, MEL, and NC homogeneously.

2.2. Specimen preparation

At first, the surface of the HDPE granules was coated with PDMS by pre-mixing with mechanical stirrer (Heidolph, RZR 2021) at 200 rpm for 5 min after the additives and nanoclay were added and mixed with mechanical stirrer again at 200 rpm for 5 min the proportions of which were given in Table I. Then the mixtures were dried at 100 °C for 2 h at oven. Dried mixtures were compounded in a twin-screw extruder (Plasti-Corder PL2000, Brabender) at 170–180–190–200 °C temperatures from feeding zone to nozzle zone at 50 rpm screw speed and the L/D ratio was 18:1. The melt blended mixtures were cooled down in water bath and cut into pellets. The extruded pellets were dried at room temperature for 48 h to remove the water and left at 100 °C for 3 h also to remove the moisture. Then those pellets were injected into mold at 160–170–180–190 °C temperatures from feeding zone to nozzle zone. Screw diameter was 35 mm and L/D ratio was 30. 20 pcs specimen groups were produced from each mixture. One group included specimens for tensile test, tear test, three-point bend test, UL94 test, cone calorimeter test, notched and unnotched Izod impact test.

2.3. Tests and characterization

All the specimens were kept for 40 h at 23 °C and 50% relative humidity before the experiment. Dimensions and weights of the specimens were measured and their densities were calculated by the ratio of mass/volume. Five specimens were used for each test and their values were averaged. The mechanical properties were evaluated by tensile test (ASTM D-638, type IV), three-point bend test (ASTM D-790), tear test (ASTM D-624, type-T), hardness test (ASTM D-2240, Shore D), the Izod impact test (ASTM D-256, notched and unnotched). Tear tests were carried out on Tinius Olsen H10KT universal test equipment at a speed of 50 mm/min. Tensile and three-point bend tests were carried out at Instron 8801 universal testing machine. Tensile test crosshead speed was 50 mm/min at room temperature. The Izod impact tests were performed with a 7.5 J hammer on the Ceast Resil Impactor device. Hardness tests were carried out with X.F Shore-D durometer. The coefficient of linear thermal expansion (CLTE) were obtained by using Linseis DMA-L77 dynamic mechanical analysis device. Specimens were cut into $10 \times 3 \times 3$ mm^3 rectangular shape which were perpendicular to the injection direction. Three specimens were used for each mixture and results were averaged. Measurements were made with quartz expansion probe at temperature range of 20 to 90 °C. Heating rate and normal load were 5 °C/min and 0.05 N, respectively. It included two heating-cooling cycles. CLTE values were calculated from second heating cycle.

3. Results and discussion

Proportion of composites in wt%, abbreviations, density, hardness, CLTE, and tear strength values are given in Table I. Densities of MEL, APP, and NC were about 1.573 g/cm^3, 1.900 g/cm^3, and 2 g/cm^3, respectively. Pure HDPE density was about 0.894 g/cm^3. The density values were increased with the addition of APP, MEL, and NC as their density values are higher than pure HDPE (Fig. 1a). Also, addition of these additives and fillers increased the hardness values of these composites (Fig. 1a). NC increased hardness by 3% compared to pure HDPE. The addition of only PDMS decreased hardness values of pure extruded HDPE slightly. APP and MEL addition decreased the CLTE and tear strength values (Fig. 1b). Tear strength values were decreased apparently by the addition of MEL. Tensile test, three-point bend test, and the Izod impact test results are given in Table II. Tensile tests were performed to determine the tensile strength, elongation, and young modulus. Extrusion process and PDMS increased the elongation values by 37% and 28%, respectively, compared to pure HDPE.

TABLE I

Composition of blends and composites in wt%, density, hardness, CLTE and tear strength values.

Abbreviation	HDPE [%]	APP/MEL [%]	PDMS [%]	NC [%]	Density [g/cm^3]	Hardness [Shore D]	CLTE [μm/(m °C)]	Tear strength [N/mm]
HDPE	100	–/–	–	–	0.894 ± 0.011	64.4 ± 1.5	140 ± 2	116.8 ± 5.9
HDPE-Ext	100	–/–	–	–	0.878 ± 0.01	64.2 ± 1.5	153 ± 2	119.9 ± 7.2
HDPE-PDMS	98	–/–	2	–	0.882 ± 0.007	63.8 ± 0.5	147 ± 12	121.6 ± 3.9
HDPE-20APP	78	20/–	2	–	0.967 ± 0.009	65.8 ± 0.5	128 ± 12	101.3 ± 3.9
HDPE-20APP3MEL1	78	15/5	2	–	0.957 ± 0.012	67.6 ± 0.5	123 ± 8	66.7 ± 7.3
HDPE-20APP2MEL1	78	13.33/6.67	2	–	0.953 ± 0.011	67.2 ± 1	127 ± 9	51 ± 3.6
HDPE-NC	96	–/–	2	2	0.881 ± 0.006	66.6 ± 0.5	136 ± 8	109.5 ± 3.6
HDPE-20APPNC	76	20/–	2	2	0.957 ± 0.026	66.8 ± 1	128 ± 9	104.4 ± 1.9
HDPE-20APP3MEL1NC	76	15/5	2	2	0.966 ± 0.013	67.6 ± 0.5	118 ± 3	45.6 ± 0.3
HDPE-20APP2MEL1NC	76	13.33/6.67	2	2	0.965 ± 0.012	67.6 ± 0.5	118 ± 6	46.9 ± 0.5

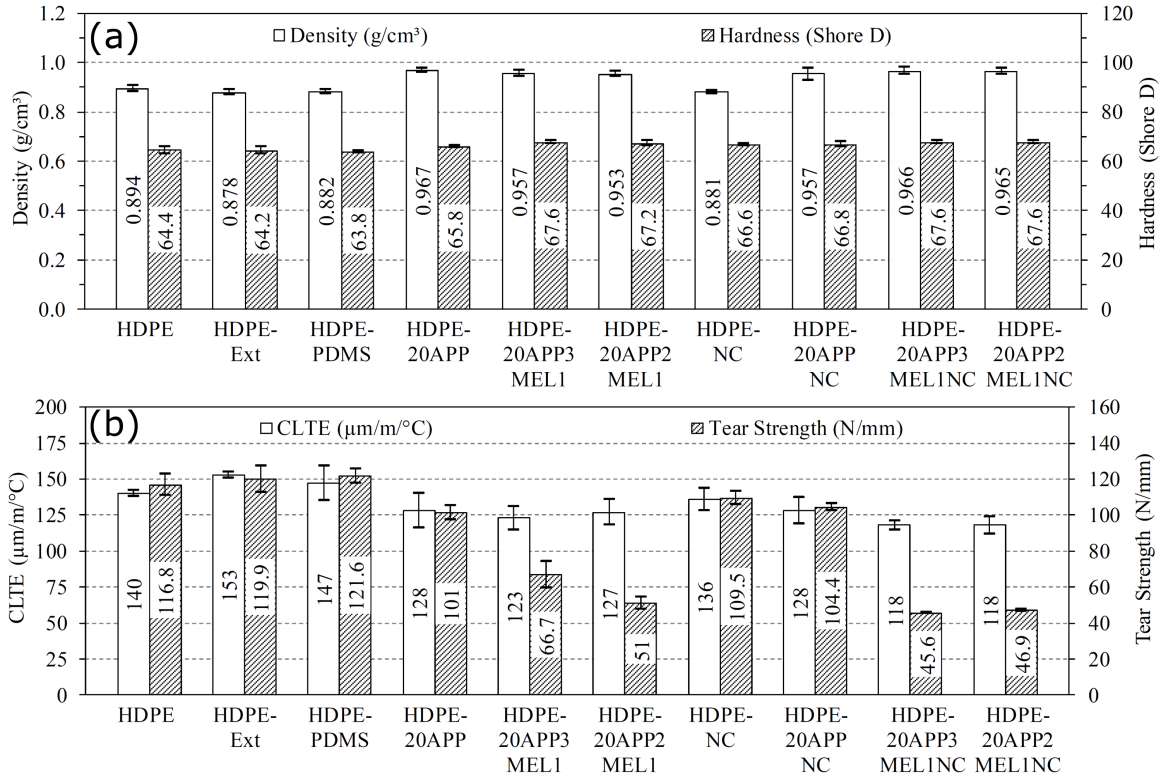

Fig. 1. Comparison (a) density–hardness and (b) CLTE–tear strengths.

TABLE II

Tensile, flexural, tear and the Izod impact test results.

Abbreviation	Tensile strength [MPa]	Young modulus [MPa]	Elongation [%]	Flexural strength [MPa]	Flexural modulus [MPa]	Impact strength [kJ/m^2]	
						Notched	Unnotched
HDPE	34.1 ± 0.9	463 ± 31	400 ± 29	30.1 ± 1.4	1109 ± 53	6.19 ± 0.25	NB*
HDPE-Ext	31 ± 0.2	440 ± 20	550 ± 50	31.1 ± 1.3	1065 ± 56	7.4 ± 0.04	NB*
HDPE-PDMS	28.1 ± 0.8	443 ± 21	514 ± 21	29.2 ± 1.1	1063 ± 43	7.02 ± 0.18	NB*
HDPE-20APP	27.8 ± 0.7	445 ± 28	80 ± 10	31.1 ± 1	1274 ± 36	4.53 ± 0.05	79 ± 6
HDPE-20APP3MEL1	28.5 ± 0.9	435 ± 25	48 ± 8	29.3 ± 1	1339 ± 17	4.4 ± 0.08	35 ± 3
HDPE-20APP2MEL1	27.3 ± 0.6	418 ± 33	54 ± 6	30 ± 0.9	1261 ± 41	4.61 ± 0.23	29 ± 3
HDPE-NC	28.4 ± 0.9	401 ± 27	197 ± 30	31.4 ± 1.2	1169 ± 29	5.73 ± 0.15	NB*
HDPE-20APPNC	28.2 ± 1.2	426 ± 30	149 ± 39	29.1 ± 1.1	1323 ± 13	4.61 ± 0.09	51 ± 9
HDPE-20APP3MEL1NC	28 ± 1	421 ± 26	46 ± 8	31 ± 0.9	1153 ± 14	4.41 ± 0.1	28 ± 7
HDPE-20APP2MEL1NC	27.2 ± 0.7	407 ± 20	38 ± 7	30.8 ± 1.1	1143 ± 37	4.41 ± 0.03	24 ± 1

*Unnotched specimen not break, NB

However, the addition APP, MEL, and NC apparently caused decrease (Table II). Tensile test results showed that extrusion process decreased the tensile strength and young modulus values by 9% compared to pure HDPE (Fig. 2a). Also, the addition of PDMS to HDPE caused decrease by 9%, compared to pure extruded HDPE. The addition of APP to HDPE decreased the tensile strength slightly whereas there was no change in young modulus compared to HDPE-PDMS. MEL and APP addition slightly increased the tensile strength at the ratio of APP/MEL (3/1) despite decrease in APP/MEL (2/1). The addition of NC to HDPE increased the tensile strength but decreased the young modulus slightly.

Three-point bend tests were done to observe the flexural strength and flexural modulus. PDMS addition decreased the flexural strength values by 3% but extrusion process increased by 3%. The highest value of flexural modulus was reached by the HDPE-20APP3MEL1. APP and NC increased the flexural modulus in contrast to MEL decrease (Fig. 2b). The Izod impact tests were performed to determine the brittleness of produced composites. The unnotched HDPE, HDPE-Ext, HDPE-PDMS, and HDPE-NC specimens were not broken but the other samples were broken. The addition of APP, MEL, and NC decreased the impact strength values. Extrusion process and PDMS increased the impact strength values by 20% and 13% in notched specimens, respectively (Fig. 3).

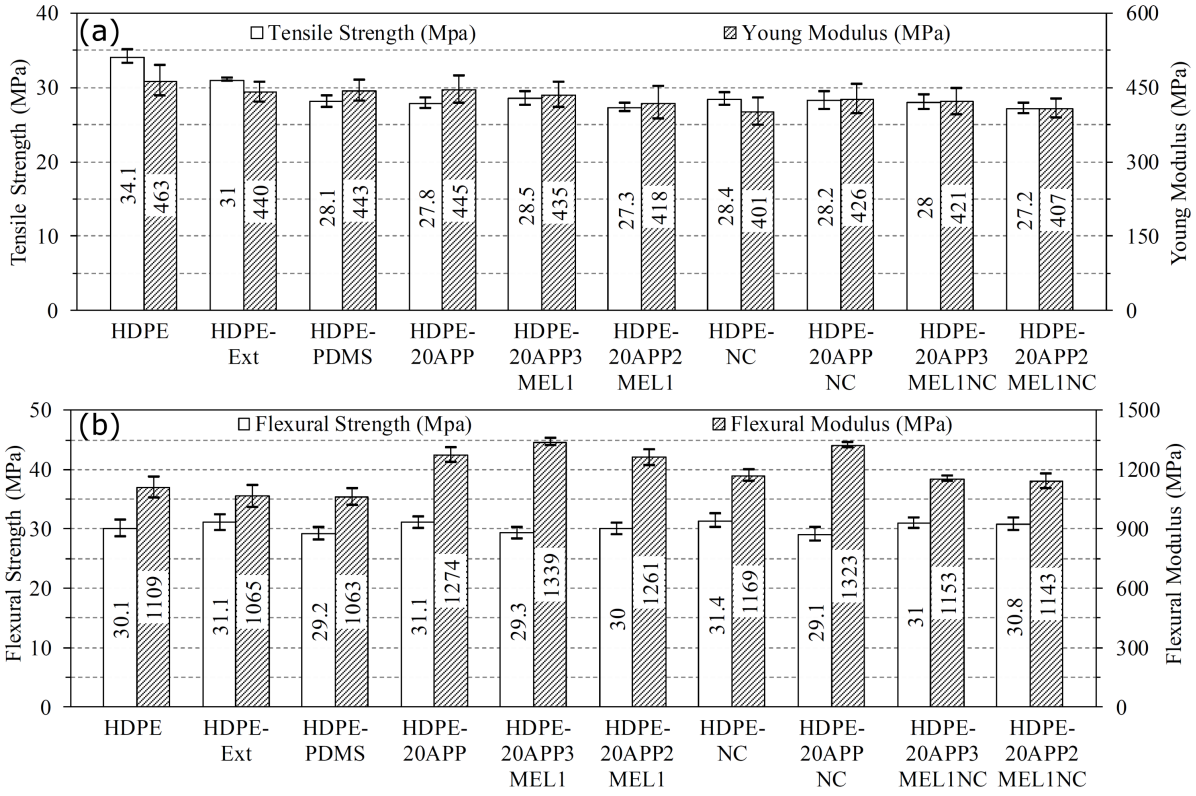

Fig. 2. Comparison (a) tensile strength–Young modulus and (b) flexural strength–flexural modulus.

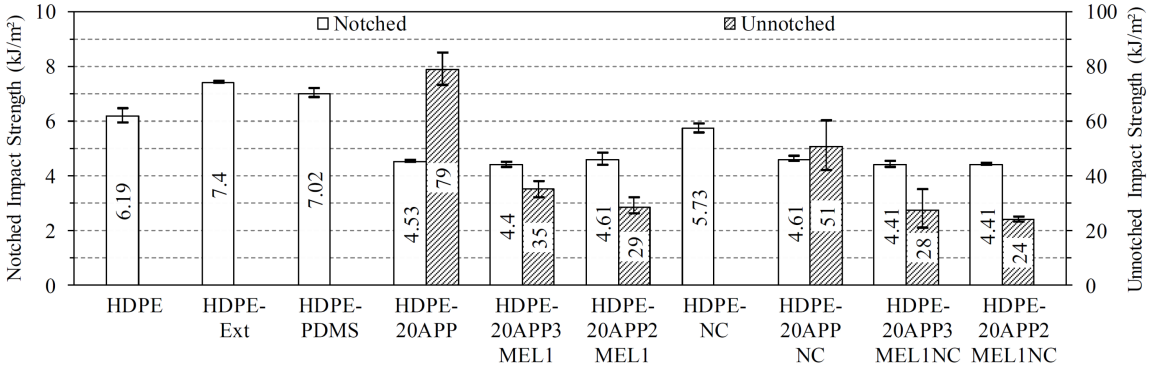

Fig. 3. Comparison of the Izod impact strengths of notched and unnotched specimens.

4. Conclusion

The addition of intumescent flame retardants and nanoclay to polymer increased the density and the hardness of polymer composites. Intumescent flame retardants and nanoclay decreased the CLTE values of composites whereas extrusion process and PDMS addition increased the CLTE values compared to pure HDPE. MEL addition dramatically deteriorated the tear strengths. Extrusion process decreased the tensile strength and Young modulus, but increased the flexural strength of composites. The addition of intumescent flame retardants and nanoclay increased the flexural modulus despite the reduction of the Young modulus. Unnotched HDPE, HDPE-Ext, HDPE-PDMS, and HDPE-NC specimens were not broken but other specimens were broken. Extrusion process and PDMS addition increased the notched impact strength while addition of APP and NC caused decrease.

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