Effect of MgOH/TiO₂ on flame retardancy and mechanical behavior of composite

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Abstract
Flame retardancy and mechanical properties of thermoplastic composites containing magnesium hydroxide (MH) and titanium dioxide (TiO₂) were investigated. Low-density polyethylene (LDPE) and ethylene-vinyl acetate (EVA) blend was incorporated with flame retardants (FRs) MH and TiO₂ in different wt.% ratios. Effect of flame retardants on fire resistance and mechanical properties of composites were characterized through UL94, limiting oxygen index, thermogravimetric analysis, tensile and impact tests. The flame retardancy was improved to V-0 with LOI value 24.9% due to the synergistic effect of both FRs. The thermal gravimetric analysis showed that the mass residue obtained was increased from 5 wt% to 25 wt%. Mechanical properties such as tensile strength and modulus of LDPE/EVA was improved from 6.4 MPa to 7.1 MPa and 127 MPa to 133 MPa respectively after the incorporation of both FRs. Impact energy absorbed was also improved from 27.8 KJ mm⁻² to 35.2 KJ mm⁻².

Introduction
Thermoplastics used in the cable industry have properties that bring long term service under different conditions. Thermoplastics are used as a coating material for cables and wires. The coating provides insulation to wire from moisture, energy dissipation, and fire. Moreover, thermoplastic coating imparts flexibility, strength, fatigue resistant and increases durability [1]. However, thermoplastics lack in fire resistance and without flame retardancy, thermoplastics undergo different types of deformations such as sponge structure formation and dripping. When thermoplastic materials are exposed to fire or high temperature, mechanical properties decreased due to polymer degradation. The structure losses its durability and collapse causing serious injuries [2]. Incorporation of flame retardants (FRs) in the thermoplastics increases the flame retardancy. FRs are of two types: additive types include physical mixing of two components and reactive type involves a reaction between two components. The most commonly used materials are metal hydroxides, nitrogen, phosphorus, silicon, polyimide and polyamide compound [1, 3–5]. These compounds prevent the high-temperature transmission between heat element and polymer material and reduce the smoke content during process of combustion. On catching fire, FR material retards or self-extinguish. FR works on different mechanisms such as thermal shielding mechanism (solid phase), endothermic degradation, gas-phase radical quenching and dilution of the gas phase. Intensity, time period and magnitude define the rate and extent of fire. The FR compounds prevent the high-temperature transmission between heat element and polymer material thus reduce smoke content during process of combustion. Different inorganic, as well as organic materials, have tendency to retard fire [6]. During thermal decomposition, metal hydrates for example magnesium hydroxide (MH) release water which absorbs heat and lets the burning material cool down and form insulation towards the fire by converting into metal oxides [3, 7, 8]. It is smoke suppressant and non-toxic flame retardant that decomposes after 310 °C [3–5, 9, 10]. Titanium dioxide (TiO₂) is a soft solid and melts at 1800 °C. It is also used as a flame retardant in different heat applications. It reduces the flame spread rate [11].

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EVA is mostly used for cable sheathing, wire applications and replacing PVC because EVA is environment-friendly, non-toxic and health hazards are minimum during its processing. Blends of EVA and low-density polyethylene (LDPE) were prepared with the addition of two different FR materials, one is magnesium hydroxide and the other is titanium dioxide at different concentrations. Prepared blend composites with FRs were then evaluated by their flame retardancy and mechanical behavior. Magnesium Hydroxide was chosen for their non-toxicity, environment-friendly nature and for their special characteristics as char producing and metal hydrates as suppressing flame retardants respectively [10, 12–14]. TiO₂ produces char to cover sample by creating a barrier [15].

Materials and method

Commercial grade LDPE and EVA were purchased from local vendor 'Tariq Plastic, Lahore'. Magnesium hydroxide (MH) and Titanium dioxide (TiO₂) were purchased from Sigma Aldrich with 99% purity.

LDPE and EVA were blended together with different compositions of MH and TiO₂ in Brabender mixer and 10 samples were prepared. Composition information is given below in table 1. S1 was composed of EVA/LDPE with a 30:70 ratio. Other samples were reinforced with MH and TiO₂ each. 3 samples were prepared using both FRs. These samples were compounded at 150 °C, 100 rpm for 10 mins. The samples obtained from Brabender mixer were compression molded at 100 °C, 1000 psi and fabricated a plain sheet of 2 mm thickness. The samples were cut according to UL 94 and ASTM standard for mechanical testing.

Characterization

The vertical burning test of all the prepared samples was conducted in accordance with the UL-94 test. All the specimens were cut in the dimensions of 120 mm × 15 mm × 2 mm. Each specimen was placed in a vertical position in a closed glass box and total time to burn the sample was recorded.

Thermogravimetric analysis of prepared composite samples was performed on a TGA-50 instrument from Shimadzu, Kyoto, Japan. 10 mg of the composite sample was placed in a standard ceramic pan and was heated at a rate of 10 °C min⁻¹ in a nitrogen atmosphere with a flow rate of 20 ml min⁻¹, from room temperature to 700 °C.

Limited oxygen index (LOI) test was performed by using a JF-4 oxygen index instrument (Jiangning Analysis Instrument Company, China) on the specimen of dimensions 120 mm × 6.5 mm × 3 mm according to the standard ASTM D2863-77.

The tensile test of FR composite was performed as per ASTM D-638 on the Z100 universal testing machine (Zwick/Roell Instruments, Germany) with sample dimensions of 20 mm×10 mm×2 mm.

Impact test was performed on the HIT50P pendulum impact testing machine (Zwick/Roell Instruments, Germany) with sample dimensions of 80 mm×10 mm×2 mm.

Results and discussions

Flame retardant analysis

Figure 1 shows the UL 94 rating of different samples. LDPE was reinforced with EVA in the 70:30 ratio (S1). The ratio kept the same for other samples with the addition of two flame retardants magnesium hydroxide (MH) and titanium dioxide (TiO₂). S1 was exposed to fire and it was seen that it did not sustain and dripping was seen. It took 1 min to burn completely. S1 was modified with 5 wt% of MH. S2 showed resistance to fire up to 1 min but

| Sample no. | Sample name | EVA (parts) | LDPE (parts) | MH (parts) | TiO₂ (parts) |
|------------|-------------|-------------|-------------|------------|--------------|
| 1          | S1          | 30          | 70          | 0          | 0            |
| 2          | S2          | 30          | 70          | 0          | 5            |
| 3          | S3          | 30          | 70          | 7          | 0            |
| 4          | S4          | 30          | 70          | 0          | 9            |
| 5          | S5          | 30          | 70          | 0          | 7            |
| 6          | S6          | 30          | 70          | 0          | 7            |
| 7          | S7          | 30          | 70          | 0          | 5            |
| 8          | S8          | 30          | 70          | 0          | 5            |
| 9          | S9          | 30          | 70          | 7          | 7            |
| 10         | S10         | 30          | 70          | 9          | 9            |
then started to burn and dripping was observed. It took 1 min and 30 sec to burn completely. Further addition of MH increases the ability to resist fire. S3 resisted fire for 1 min and dripping was observed. It started burning for 1 min 50 sec. Both samples showed a V-2 rating. S4 showed better performance. It resisted fire up to 1 min and no dripping was observed. It took 2 min 30 sec to burn completely. This is because MH is smoke suppressant and non-toxic flame retardant. During combustion MH produces endothermic reaction, which releases water, absorbs heat to cool down the burning material hence proves it to be smoke suppressing agent and form insulation towards the fire by converting into metal oxides [16].

Further samples S5, S6, and S7 were prepared by using TiO2 as a flame retardant. S5 showed resistance to fire up to 50 sec but then started to burn and dripping was observed. It took 1 min and 13 sec to burn completely. Further addition of TiO2 increases the ability to resist fire. S6 resisted fire for 1 min and dripping was observed. It started burning for 1 min 45 sec. Both samples showed a V-2 rating. S7 showed better performance. It resisted fire up to 1 min and no dripping was observed. It took 2 min 40 sec to burn completely.

Then samples S8, S9 and S10 were prepared and both MH and TiO2 were added in LDPE/EVA composite. A synergistic effect was observed. S8 resisted fire for 1 min 20 sec and no dripping was observed. It shows a V-2 rating. S9 and S10 resisted fire for 2 min and no dripping was observed. It shows V-0 rating. It was seen that TiO2 improved the fire-resistance by producing char. The honeycomb structure char covered the whole material to resist fire.

**Thermogravimetric analysis**

Figure 2 shows the thermogravimetric curves of the LDPE/EVA blend and its composites with FR. The curves explain the thermal degradation characteristics of samples. Weight loss at maximum thermal decomposition temperature (T\text{max}) char yields at 600°C and temperature (T) at 5% weight loss.

Thermal properties of all formulations are compared at two different temperatures, first is temperature (T) at 5% weight loss and second is at 600 °C to observe char yields or mass residue. S1 shows a narrow thermal decomposition plateau in a range of 0 °C to 80 °C with 5 wt% mass loss as shown in figure 2. S1 is a thermoplastic polymer, therefore, exhibits lower thermal stability up to 410 °C. S1 mass residue obtained is 5 wt% at 600 °C. Sample S2 and S3 were not tested for thermogravimetric analysis because very small quantities of FR were added in them and UL 94 rating obtained was not up to the mark, therefore, it’s not worth to test TGA. S4 shows 5% weight loss at 100 °C which is almost same as the curve of S1. However char yield 9.5% at 600 °C. This is because of the MH addition which hindered the complete burning of the composite, hence increased mass residue to 9 wt%. The sample was saved by breaking the compound (MH) endothermically when exposed to high temperatures and suppress the smoke and fire. MH often comes out of material when exposed to flame. S7 shows a 5% weight loss at temperature of 376 °C. This is due to higher concentration of TiO2 that shows high degree of stability. The char yield at 600 °C is 10.3 wt%. S8 exhibits 5% weight loss at temperature of 376 °C. This is due to synergistic effect of MH and TiO2 added at high concentration levels. S8 shows high degree of stability. However the char yield at 600 °C is 3 wt%.

The curve of S9 and S10 shows almost the same values up to 420 °C and char yield 15 wt% and 20 wt% respectively. The mass residue obtained was increased from 5 wt% to 25 wt%. This is because of the synergistic
effect of both FRs. It can be observed that both FRs start affecting the performance and increased thermal stability. Both FRs work on the same mechanism i.e. removes heat from the system hence improve the fire resistance.

**Limiting oxygen index (LOI)**
The effect of MH and TiO₂ on the LOI value of LDPE/EVA/MH/TiO₂ composites is shown in figures 3, 4 and 5. When the no FR was added in it S1 shows LOI 19.7%. However, addition of MH content in S2, S3, S4 increases from 5 wt% to 9 wt%, a slight increase in LOI is observed. It can be seen that high concentration of MH improved it up to 22% as shown in figure 3. The reason for this is that MH is flame-retardant material. Similarly, addition of TiO₂ content in S5, S6, S7 increases from 5 wt% to 9 wt%, an increase in LOI is observed. It can be seen that high concentration of TiO₂ improved it up to 22.8% as shown in figure 4. The sample S8, S9, and S10 had both FRs in equal wt%. It can be observed that synergistic effect improved the LOI values from 23.0% to 24.9% as shown in figure 5. This indicates that the addition of FR can improve the flame retardancy of LDPE/EVA/MH/TiO₂ composites.

**Mechanical analysis**
The tensile test was performed and stress-strain (SS) curves are shown in figure 6. Young’s modulus, tensile strength, and elongation at break also mentioned in table 2 for all samples. Impact strength results also shown in
It is clear that sample S1 has the lowest tensile strength and elongation as shown in Fig. 3. FR goes in between the chains, provides empty space for the chains to easily move and disentangle when the force is applied. By increasing FR (MH) amount, Elongation at break continuously increased from 75% for S1 to 130% for S4. Tensile strength also seems to increase from 6.4 MPa to 7.3 MPa most probably due the chain restriction by the filler particles that need more stress to move from their position when stress is applied. A similar trend was also observed for samples S5 to S7. By adding 9% TiO$_2$, all parameters i.e. tensile strength, impact strength, elongation at break, etc were reduced to minimum value as TiO$_2$ agglomerates and have no compatibility with polymers. From sample S8 to S10, both MH and TiO$_2$ were added in same composition, due to high filler content and agglomeration, elongation at break reduce to minimum value and strength reduce to a moderate value.

It was also observed through an impact test that energy absorbance property of EVA/LDPE was also enhanced from 127 KJ mm$^{-2}$ to 133 KJ mm$^{-2}$. Impact strength graph is shown in Fig. 7. Intercalation, chain entanglements, filler/polymer interaction, and free space are the main reasons for enhancement in both tensile and impact properties.
Figure 6. Stress-Strain Curves of Prepared Samples.

Table 2. Young's modulus, tensile strength and elongation at break of prepared samples.

| Sample name | Young's modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) |
|-------------|----------------------|------------------------|-------------------------|
| S1          | 127.7                | 6.4                    | 75                      |
| S2          | 121.4                | 6.9                    | 127                     |
| S3          | 126.7                | 7.0                    | 100                     |
| S4          | 134.5                | 7.3                    | 130                     |
| S5          | 124.3                | 6.7                    | 70                      |
| S6          | 138.6                | 6.9                    | 132                     |
| S7          | 109.4                | 7.9                    | 88                      |
| S8          | 123.6                | 7.1                    | 35                      |
| S9          | 121.9                | 6.5                    | 70                      |
| S10         | 133.1                | 7.1                    | 74                      |

Figure 7. Impact strength of Prepared Samples.
Conclusion

Effect of MH/TiO$_2$ on flame retardancy and mechanical behavior of composite were analyzed in this research work. Flame retardancy test of samples was carried out in accordance with UL-94 standard, it was seen EVA/LDPE blend was completely burnt however upon addition of FRs the samples showed an improved rating from V-2 to V-0. The effect of FRs was also checked separately. Both MH and TiO$_2$ addition improved the fire resistance to V-1 when mixed separately in EVA/LDPE blend. In synergistic effect, both FR materials improved flame-retardant property to V-0. The LOI was increased from 19.7% to 24.9%. The stress-strain curve shows the ductile behavior of the composite. Moreover by incorporating the flame retardants the mechanical properties of the composites were also improved.

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References

[1] Larché J et al 2014 Evidence of surface accumulation of fillers during the photo-oxidation of flame retardant ATH filled EVA used for cable applications Polym. Degrad. Stab. [Internet]. 103 63–8
[2] Ayirimis N et al 2012 Effect of boron and phosphate compounds on physical, mechanical, and fire properties of wood-polypropylene composites Constr. Build. Mater. 33 63–9
[3] Rothon R N N and Hornsby P R R 1996 Flame retardant effects of magnesium hydroxide Polym. Degrad. Stab. 54 383–5
[4] He D et al 2017 Flame retardancy and toughening properties of epoxy composites containing ammonium polyphosphate microcapsules and expanded graphite High Perform. Polym. 30 09540831774795
[5] Wang J et al 1996 Microstructure and mechanical properties of ternary phase retardant compositions J. Appl. Polym. Sci. 60 1425–37
[6] Stark N M et al 2010 Evaluation of various fire retardants for use in wood flour-polyethylene composites Polym. Degrad. Stab. 95 1903–10
[7] Sain M et al 2004 Flame retardant and mechanical properties of natural fibre—PP composites containing magnesium hydroxide. 83 363–7
[8] Yang J, Liang J Z and Tang C Y 2009 Studies on melt flow properties during capillary extrusion of PP/Al(OH)$_3$/Mg(OH)$_2$ flame retardant composites Polym. Test. [Internet]. 28 907–11
[9] Jadhav S D 2018 A review of non-halogenated flame retardant Pharma Innov. 1 7 380–6
[10] Yanyan D, Liang X U and Gengsheng H U 2011 Performance of halogen-free flame retardant EVA/MH/LDH composites with nano-LDHs and MH 56 878–83
[11] Lam Y L, Kan C W and Yuen C W M 2011 Effect of Titanium Dioxide on the Flame-Retardant Finishing of Cotton Fabric 121 267–78
[12] Larché J F et al 2014 Evidence of surface accumulation of fillers during the photo-oxidation of flame retardant ATH filled EVA used for cable applications Polym. Degrad. Stab. 103 63–8
[13] Zhang X et al 2005 Investigation of interfacial modification for flame retardant ethylene vinyl acetate copolymer/alumina trihydrate nanocomposites Polym. Degrad. Stab. 87 411–8
[14] Riva A et al 2003 Fire retardant mechanism in intumescent ethylene vinyl acetate compositions. 82 341–6
[15] Li H et al 2013 Progress in organic coatings effects of titanium dioxide on the flammability and char formation of water-based coatings containing intumescent flame retardants Prog. Org. Coatings [Internet]. 78 519–24
[16] Cao R, Deng Z L, Ma Y H and Chen X L 2017 Effect of EVA on thermal stability, flammability, mechanical properties of HDPE/EVA/Mg(OH)$_2$ composites Materials Science and Engineering 213 012002