Evaluation of the Epoxy/Antimony Trioxide Nanocomposites as Flame Retardant

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Abstract. Antimony trioxide nanopowder was added for epoxy resin in various amount weight percentages (0, 2, 4, 6, 8, and 10) wt% to increase the combustion resistance and decrease the flammability for it. The study included three standard tests used to measure: limiting oxygen index (LOI), rate of burning (R.B), burning extent (E.B), burning time (T.B), maximum flame height (H) and residue percentage after burning in order to determine the effectiveness of the used additives to decrease the flammability of epoxy resin and increase the combustion resistance. Thermal test was done by using Lee’s disk to measure the thermal conductivity coefficient. The thermal stability and degradation kinetics of epoxy resin without reinforcement and with reinforcement by (10 wt%) were studied by using thermogravimetric analysis (TGA). The recorded results indicated that epoxy reinforced by (10 wt%) has a good effect as flame retardants for epoxy resin and active to inhibit burning and reduce the flammability.

Keywords: Flame Retardant, Antimony Trioxide Nanopowder, Composite Material, Epoxy Resin and Inorganic Retardants.

1. Introduction
Flame retardants are defined as chemical materials that have the ability to withstand direct flame where it works to increase ignition resistance and reduce rate of flame spread and it is added to the material that doesn't have the ability to resist flame to improve its properties [1-3]. These materials are either additives called external flame retardants, which are an ineffective chemical additives added and mixed with polymeric materials without any chemical reaction with them, or as part of the polymer structure called the internal flame retardants[4].

Two methods are known to inhibit the flame, the first method is preventing the oxygen from reaching to flame zone by generating non-combustible gases which cause poisoning the flame by free radicals and extinction it, the second method depends on the thermal flame theory which states that the flame retardants need to thermal energy to disintegrate which leads to the reduction of the heat surface material to temperature less than the temperature of ignition and thus the burning will stop [5-7].

There are four primary materials which work to retard flame in various ways. These materials include nitrogen, phosphorus, halogenated and inorganic flame retardants [8,9].

Antimony trioxide is an inorganic compound with the formula Sb2O3, which has stability in high temperatures so it is used as a flame retardant in engineering materials.
Antimony trioxide has chemical formula (Sb2O3) or (Sb4O6) depending on its internal structure, where the cubic structure is colorless, while the orthorhombic structure is white. The cubic antimony trioxide is stable under temperature 570ºC and the orthorhombic is stable above temperature 570ºC [10].

The aim from this study is manufacture flame retardant composite material by adding nano antimony trioxide which was used as flame retardants to epoxy resin to increase the combustion resistance and decrease the flammability for it

2. Experimental Part

2.1. Materials

2.1.1. Polymer

Epoxy resin and hardener type (amine), imported from Sikadur-52 company, USA. Epoxy and hardener were used in this study in ratio of (2:1) for curing.

2.1.2. Flame retardant

Antimony trioxide nanopowder is supplied from Hongwu International Group Ltd, China with purity 99.5%, particles size (20-30) nm and orthorhombic phase (Valetinite) which have white color.

2.2. Synthesis

The samples of flame retardancy are formed by hand lay-up molding. Molded samples are a sheets shape in the dimensions of (13x13x0.3) cm. These sheets of epoxy resin were prepared for each percentage weight (0, 2, 4, 6, 8 and 10%) of flame retardant materials (antimony trioxide nanopowder), then the samples are cut by laser and have smooth edges according to the tests method. For limiting oxygen index (L.O.I), rate of burning (R.B) and maximum height of flame (H) testing, the specimens were chosen and each one has a length of ((130 ± 5), (130 ± 5) and (125± 5)) mm, width of ((6.5 ± 0.5), (12.5 ± 0.5) and (10 ± 0.1)) mm, respectively and thickness of (3.0 ± 0.1) mm. The specimens for thermal conductivity testing were a tablet shape and each one that has a width of (40 ± 0.2) mm and thickness of (4.0 ± 0.1) mm. The weight of samples for thermogravimetric analysis (TGA) testing was 17gm.

2.3. Characterization

The flammability of polymers was determined by limiting oxygen index (L.O.I) (ASTM: D-2863). The rate of burning (R.B), average extent of burning (A.E.B) and average time of burning (A.T.B) are measured according to (ASTM: D-635). The maximum height of flame (H) and the amount of loss in weight of polymer are measured according to (ASTM: D-3014). The thermal conductivity coefficient was estimated by Lee’s disk test. The thermal degradation was studied using thermogravimetric analysis which carried out by (differential scanning calorimetry), model STA PT-1000 linseis, Germany.

3. Result and Discussion

3.1 Limiting oxygen index (L.O.I) test

L.O.I is the most widely used test to determine the flammability of polymer. It was measured by (ASTM: D-2863) method and calculated from the following equation[11]:

\[ n\% = \frac{O_2(O_2+N_2)^{-1/2}}{100} \]  

Where:

- \( n\% \): limited oxygen index.
- \( O_2 \): volumetric speed flow of oxygen (ml / sec).
N₂: volumetric speed flow of nitrogen (ml/sec).

The results obtained are represent in table 1, and show the L.O.I increased with the increase of the reinforcement ratios (directly proportional).

| Type of additive | Additives% |
|------------------|------------|
|                  | Non  | 2    | 4    | 6    | 8    | 10   |
| Sb₂O₃            | 19.59| 21.18| 22.17| 22.7 | 23.07| 23.8 |

The limiting oxygen index (L.O.I) increased with the increase of the reinforcement ratios is due to the release of the oxygen root, which works to remove the active free radicals in the flame chain and inhibit the process of thermal fragmentation that occurs at the outset of the flame because of its effect in reducing the amount of heat generated by the flame.

3.2. Rate of burning (R.B) test

A.T.B in minutes and A.E.B were measured by (ASTM: D-635) method and calculated from the equations (2) and (3), respectively [12]:

\[ \text{ATB} = (\sum(t-30)) \text{ (No. of samples)}^{-1} \] (2)

\[ \text{ABE} = (100-X) \text{ (No. of samples)}^{-1} \] (3)

Where

- t: time of burning (min).
- X: length of the unburned part of the model when self-extinguishing occurs (cm).

Others variables were calculated from (ASTM: D-635) method in addition to A.E.B are:

- R.B: rate of burning (cm/min).
- S.E: self extinguishing.
- N.B: the ignition non continuity of the specimen after the removal of heat source.

The result obtained from these tests showed that, the rate of burning of the epoxy resin with the additives has a continuous reduction with the increase of the percentage weight of additives, as in table 2, which showed the flame speed curves of flame retardation for resin.

| Test | Additives % |
|------|-------------|
|      | Non  | 2    | 4    | 6    | 8    | 10   |
| A.T.B| 5.35 | 6.71 | 7.3  | 3.22 | 2.52 | 2.25 |
| A.E.B| 10.3 | 10.3 | 10.3 | 4.1  | 1.8  | 1.4  |
| R.B  | 1.92 | 1.73 | 1.69 | 1.2  | 0.57 | 0.49 |
| S.E  | -    | -    | -    | Yes  | Yes  | Yes  |
| N.B  | -    | -    | -    | -    | -    | -    |

The rate of burning (R.B) decreased with the increase of the reinforcement ratios due to the formation of non-flammable gases such as (CO) reduces flammable volatile substances and provides an inert atmosphere that forms a cover between oxygen and the burned area where it prevents or reduces oxygen from reaching the flame. Char, which is former of thermal decomposition, forms a barrier that protects the polymer from heat.
3.3. Maximum height of flame (H) test
The weight percentage for the residual of the burning material was measured by (ASTM: D-3014) method and calculated by the following relationship [13]:

\[ PWR = \frac{(W_1 - W_2)(W_1)}{100} \]  

Where
- \( W_1 \): weight of the sample before combustion (gm).
- \( W_2 \): weight of residual material after combustion (gm).
- PWR: percentage weight of the residual of burning material.
- H: maximum height of flame reached (cm).

Table (3), show the results of the measurement of flame height for EP. with various amount weight percentages of Sb\(_2\)O\(_3\).

| Test | Additives% | Non | 2 | 4 | 6 | 8 | 10 |
|------|------------|-----|---|---|---|---|----|
| \( W_1 \) (gm) |          | 4.56 | 4.95 | 5.03 | 5.14 | 5.22 | 5.31 |
| \( W_2 \) (gm) |          | 1.37 | 1.16 | 1.24 | 1.32 | 1.36 | 1.47 |
| PWR% |          | 69.95 | 76.56 | 75.34 | 74.31 | 73.94 | 72.31 |
| H(cm) |          | 12.3 | 9.9 | 7.6 | 6 | 4.8 | 3.7 |

Table (3), revealed the most effective additive at 10% where the flame height (H) is decreased from 12.3cm to 3.7cm and shows that the flame height (H) decrease with the increase of the reinforcement ratio (inversely proportional) because of the formation of carbonaceous char, which leads to the detention of oxygen from the polymer material and thus contribute to the cessation of ignition or reduce the flame.

3.4. Thermal conductivity test
Thermal conductivity coefficient (K) was calculated by thermal conductivity test. Thermal conductivity is a measure of the ability of a materials to allow the transport of heat from warmer regions to colder regions through the material. Coefficient of thermal conductivity (K) is the amount of heat conducted per second normally across unit area perpendicular to the direction of heat conduction at unit temperature gradient. It is measured in watts per Kelvin-meter (W.k\(^{-1}\).m\(^{-1}\)) or in IP units (Btu.hr\(^{-1}\).ft\(^{-1}\).F\(^{-1}\)) [14]. Lee's disk test is one method used to determine the thermal conductivity coefficient of additives.

A value of thermal conductivity coefficient of the specimens (K) of thickness (d) and radius (r) is calculated by using the following equation [15]:

\[ K \left( \frac{T_B - T_A}{d_S} \right) = e \left[ T_A + \frac{2r}{\pi} \left( \frac{d_A + d_S}{4} \right) T_A + d_A T_B / 2r \right] \]  

Where:
- \( d_S, d_A, d_B \) and \( d_C \) : are the thickness of the sample and the disks respectively (mm).
- \( T_A, T_B \) and \( T_C \) : are the temperature of the disks A, B and C (°C).
- \( e \) : quantity of thermal energy would be emitted from exposed area of the surface (W/m\(^2\).°C) calculated by using following equation [16]:

\[ IV = \pi r^2 e \left( T_A + T_B \right) + 2\pi r e \left[ d_A T_A + d_S / 2 \left( T_A + T_B \right) + d_B T_B + d_C T_C \right] \]  

Where:
- \( V \) : is the difference potential across the heater.
- \( I \) : is the current which flows through it.
Table (4), shows the obtained results of measurements of thermal conductivity coefficient (W/m.°C) for EP. with different reinforcement ratios which increasing with the increase of the percentages of reinforcement added (directly proportional).

| Type of additive | Additives% |  |  |  |  |  |
|------------------|------------|---|---|---|---|---|
|                  | Non        | 2 | 4 | 6 | 8 | 10 |
| Sb$_2$O$_3$      | 0.37957    | 0.45171 | 0.49234 | 0.48312 | 0.44425 | 0.25773 |

This test was runned to determine the effectiveness of antimony trioxide nanopowder on thermal insulation or thermal conductivity at low temperatures where the thermal conductivity of composite material begins to rise with the increase of the reinforcement ratios, the reason for this is that the addition nano particle to polymer works to reduce the degree of cross linking between the molecular chains that give them larger freedom of movement and increase the ability to vibration movement so the heat passing through the composite material collides with the Sb$_2$O$_3$ grains that begin to absorb the heat. This absorption leads to a reduction in the passage of heat through the material, which reduces the thermal conductivity, but after a period of time and at high temperature, these grains begin to vibrate (thermal excitation) due to high temperature, and this vibration causes the heat rush through the composite material, leading to increase thermal conductivity.

The absorption of Sb$_2$O$_3$ of the heat is increased by increasing its proportion within the composite material thus it becomes a good conductor of heat.

3.5. Thermogravimetric Analysis (TGA)
Thermogravimetry (TG) is one of the thermal analysis which is used to characterize a wide variety of materials and provide supplementary characterization information to the thermal technique (DSC). It measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere [17]. In this work, TGA is used to know the thermal stability of polymers and the effect of additives on thermal stability for these polymers. ‘Figure 1’, illustrate the TGA results of EP. without additive and with (10 wt%) additive.

In two samples a change in peak was observed due to different melting behaviors of composite materials. There is no change in the starting of melting thermogram and there was a marginal increase
in the ending of it. The glass transition temperature for the pure sample is 111.5 °C and for the reinforced sample is 115.5 °C this difference is due to the nanoparticle penetrates inside the base material and works to fill and reduce the gaps that formed during the molding process, which gave better thermal properties. The weight loss at rel. mass change (98%) is due to the epoxy resin loses humidity by evaporation process and at 95% occurs because the epoxy begins to decompose.

4. Conclusions

The used additive was effective in reducing the flame and preventing the combustion of epoxy resin. The limiting oxygen index (L.O.I), thermal conductivity and thermal stability increases, rate of burning (R.B) and maximum flame height (H) decreases with the increase of the reinforcement ratios. Self extinguishing (S.E) occurred at the weight percentages (6, 8 and 10%).

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