

The effect of (glass, carbon) fiber and CNT on thermal properties for epoxy resin

Harith I. Jafer

Nadia A. Ali

Baghdad University\ college science

1. INTRODUCTION

Epoxy resins are used worldwide on a large scale for adhesive, lamination, coating, casting applications, and so forth. To meet some application requirements, several approaches have been used to enhance the thermal properties of epoxy resins. Apart from that, a further requirement that has recently gained in importance's the requirement for flame resistance. Therefore, imparting flame retardancy into epoxy resins has received a lot of attention. In order to improve the flame retardancy of pure epoxy. Resins have very harmful burning characteristics, i.e., high flammability at relatively low temperatures, very toxic and acrid smoke, and rapid destructive flame spread. It is well known that the flammability of thermoset resins can be reduced by incorporating flame retardant agents at the raw material manufacturing phase of resin, or, blended as an additive with the polymer prior to use. The burning behaviors of such materials, particularly those that are to be used in an enclosed environment, are of primary concern to end users, regulators and governing authorities. Epoxy composites are resistant to ignition and have extremely low levels of low flame spread when involved in a fire situation. These factors, combined with the minimal levels of smoke and toxic emissions that are produced in a fire. Epoxies are used in all the traditional composite processes, including wet laminating, resintransfer moulding and filament winding. Decomposition of most epoxies occurs via random chain scission reactions over the temperature range of about 380 to 450°C[1,2].

A major disadvantage of many composite materials is poor performance in fire. When composites are exposed to high temperatures (typically above 300–400°C) the organic matrix decomposes with the release of heat, smoke, soot and toxic volatiles. Composites also soften, creep and distort when heated to moderate temperature (>100–200°C), that can result in buckling and failure of load-bearing composite structures. The heat, smoke and gases released by a burning composite and the degradation in structural integrity can make fire-fighting extremely hazardous and increase the likelihood of serious injury and death[3,4].

Flame spread rate describes the speed at which the flame front will travel over the surface of a combustible material. The flame spread rates an experimentally measured value, and various experimental techniques with important differences in test configuration are used. Some tests are used to measure the rate of flame spread in a downward direction while other techniques measure it in a vertical or horizontal.

Smoke density because they have a major impact on the ability of humans to survive a fire. Smoke density is defined and measured in several ways, but basically it is the concentration of smoke particles (e.g. soot, water vapor) within the plume of a fire[5].

Flame– retardancy can be achieved using any of three different approaches:

- (1) Causing “char” formation in the pyrolysis zone.
- (2) Adding material that decomposes produce non–flammable gases or endothermic ally cools the pyrolysis zone.
- (3) Prohibiting the combustion process in the vapor phase. Many flame retardants have been developed to combat the thermal break down of polymers [6].

Fiber Reinforced Composites based on epoxy Resin systems have been used for more than 20 years with excellent results to produce moldings and laminates. They do not readily burn and if involved in a fire, produce minimal levels of smoke or toxic. One of the main safety concerns with using fibereinforced polymer (FRP) composites is their combustibility. Many polymer composites ignite when exposed to high heat, in some circumstances, contribute to the growth of the fire. Significant quantities of smoke and toxic fumes may also be released, respectively limiting visibility and posing a health hazard. For these reasons, stringent fire regulations govern the use of composites in aircraft, ships, buildings, land transport, oil and gas facilities, and other applications. These regulations require that the fire reaction properties meet specified levels. The reaction properties that are often used to define the fire hazard include the heat release rate, time–to–ignition and flame spread rate. These properties are important because they influence the temperature and spread of a fire, while the fiberglass reinforcements used in corrosion resistant laminates will not burn, most thermosetresins used as the matrix for "FRP" laminates will support combustion. Even the "fire retardant" resins will burn vigorously when fire is supported by an outside source. When combustion occurs, these additives suppress, or smother, the flame and the laminate becomes self extinguishing [7].

Carbon-fiber-reinforced polymer (CFRP) is a very strong, light, and expensive composite material or fiber-reinforced polymer. Similar to fiberglass (glass reinforced polymer), the composite material is commonly referred to by the name of its reinforcing fibers (carbon fiber). The polymer is most often epoxy, but other polymers, such as polyester, vinyl ester or nylon, are sometimes used. Some composites contain both carbon fiber and other fibers such as Kevlar, and fiberglass reinforcement. It has many applications in aerospace and automotive fields, as well as in sailboats, and notably in modern bicycles and motorcycles. Resin content generally provides the highest fire load but when used of inert fibres (glass, carbon) usually reduces overall composite flammability and Fiber/resin composite combinations are based on performance versus cost compromises[8,9].

Experimental:

Material

1-The material used to prepare the test samples was epoxy resin (EPI0 Conbextra) with the hardener aliphatic amine (Hy956) reinforced by two types of E-glass (density 2,62 g/cm³) fibers and carbon fiber (density 2.25g/cm³), Laminated sheets of different layers were prepared by hand lay-up method from the neat epoxy resin and its composites. The sheets were cut to a certain dimension specimens according to ASTM E-662 [12].

2- Epoxy and hardener were used in this study in ratio of (3:1) for curing with-wall carbon nanotubes (MWNT) CNT) (obtained by the chemical vapor deposition (CVD)) in Fig (1) and diameter 30-40 nm [13]. Composites with three different concentration of CNT (0.001%, 0.05%, and 0.1%) weight percentage. CNT was first dispersed in chloroform solution under magnetic agitation to reduce the maximum size of the aggregates to about 100 nm. After complete evaporation of chloroform the obtained CNT powder was then directly added to the epoxy resin and hardener mixture. The samples were placed between two metal plates under pressure () to get out the air. Before measurements, the surfaces of the specimens were mechanically polished to minimize the influence of surface flaws. Finally, they were cast in moulds, the specimen were cut dimensions (250mm*250mm*3mm).

3-Smoke density chamber

This test is designed to measure the density of the smoke generated as a function of time, under both flaming and smoldering conditions. Because this test was originally developed by the National Bureau of Standards (NBS), the test is

sometimes referred to as the NBS smoke density test, which contains an optical light source and detector to measure the reduction of optical density from the smoke generated by the burning of a sample placed inside the chamber. The sample is small (Results are usually expressed as a smoke density, D_s , after a 1.5 or 4.0 minutes).

$$D_s = V/LA \text{ LOG } (100/T \%) \dots\dots (1)$$

V =volume of closed chamber (cm^3)

A = is the exposed area of specimen (cm^2)

L = length of light through the smoke (cm)

T = percent light transmittance as read from the light sensing instrument (%)

Smoke density rating =total smoke density under curve /16000*100%..... (.2)

$$D_m = 240 \text{ LOG } 100/100 - \text{MSD} \dots\dots (3)$$

D_m =maximum specific optical density

MSD=maximum smoke density

4–Rate of burning (or flame speed): This parameter is measured according to the ASTM–D635 [14]. The polymer samples sheet prepared according to this method is of 12.5cm length, 1.25 cm thickness. The maximum flame height is measured by metal ruler in centimeter after 10 sec of burning process in a horizontal position, the free end was exposed to a specific gas flame for 30s or until the flame front reaches the 2.5cm from the free end., the time was recorded in second, as the burning (t°).The time was recorded , when the flame front reaches the 10.0cm from the free end , as burning time (t),if the burning has not reach the 10.0cm, measure the unburned length (x).The length of extent of burning equal to 10.0cm minus unburned length. The average of burning time could be found according to the following formula:

$$\text{ATB} = \sum (t - t^\circ) / \text{no. of specimens} \dots\dots (4)$$

t = burning time in 10.0cm

t° =burning time after 30s, or in 2.5cm

\sum =algebra sum

Average extent of burning might be found by the following formula:

$$\text{AEB}_{\text{cm}} = \sum (10.0\text{cm} - \text{unburned length} / \text{no. of specimens}) \dots\dots\dots (5)$$

$$\text{R.B} = \text{AEB}_{\text{mm}} / \text{ATB} \dots\dots\dots (6)$$

R.B=Rate of burning in cm/min

Result and Discussion

The results of this study are important to the composites industry because it is the beginning of how the (glass, carbon) content affects the overall fire performance of epoxy composites. The effect of glass or carbon content of epoxy composite is found to be less significant, there is a difference in the maximum smoke density and smoke density rating shows in Tables (1, 2). When a composite is heated to a sufficiently high temperature the polymer matrix and (if present) organic fibers will thermally decompose. Most polymer matrixes and organic fibers decompose over the temperature range of about 350 to 600°C with the production of flammable gases. Decomposition occurs by a series of reactions that breaks down the polymer chains into low molecular weight volatiles that diffuse into the flame. Depending on the chemical composition and molecular structure of the polymer, the thermal degradation reactions may proceed by various paths. The majority of organic resins and fibers [16].

Tables (1): smoke density data of Epoxy with glass fiber in different ratio

additives	Epoxy	5%G.F	10%G.F	15%G.F
total smoke density (mm ²)	8010	6730	4610	3870
maximum smoke density	62	57	47	44
Smoke density rating (mm)	50.1	42	28.8	13.7

Tables (2): smoke density data of Epoxy with carbon fiber in different ratio

additives	Epoxy	5%C.F	10%C.F	15%C.F
total smoke density (mm ²)	8010	5260	3730	2990
maximum smoke density	62	54	44	40
Smoke density rating (mm)	50.1	32.9	25.5	11.6

When thermoset resins epoxy burn it give large amounts of heavy, black, dense smoke can be generated, because the carbon chains in these resins contribute to that smoke. When used for fiberglass reinforced and carbon fiber reinforced resin composites, there is no difference in the density of the smoke generated between a non-combustible composites fibers .

Carbon fiber was environmentally neutral with a low smoke density rating and low smoke emission. It was chemically stable, prevented dripping. The material is drawn into fibers and kept under tension while it is heated under high temperature ($> 1000\text{C}$), dimensional carbon-carbon crystals (graphite) are formed when the hydrogen is driven out. The carbon-carbon chain has extremely strong molecular bonds and that is what gives the fibers its superior mechanical properties [8].

In tables (3,4) shows the values of flame speed of EP/G.F, EP/C.F. Fiber glasses their inherent fire retardant (low rate of burning) . Fiber glass is one of the few insulation types that are naturally fire resistant, and still it may melt at extremely high temperatures. It is popular because of its cost-effectiveness and energy efficiency. Fiber glass is composed of sand and recycled glass, causing it to be naturally non-combustible, although it may melt when it reaches extremely high temperatures. [11].

Tables (3,4) also shows that increase in the burning time with increase contact of (glass, carbon) and that means that additives fire retardant translation flame into polymer. The surface temperature significantly decreased with glass , carbon content for the epoxy composites[9].Flame retardants are chemical agents which are added to combustible materials to make them more resistant to ignition and they are intended to minimize the risk of a fire starting in case of contact with a small heat source used in composites degrade thermally by a random chain scission process. This basically involves the break-down of the long organic chains at the lowest-energy bond sites into small fragments[10].

Tables (3): Flame speed of Epoxy with glass fiber in different ratio

additives	Epoxy	5%G.F	10%G.F	15%G.F
AEB (cm)	2	2	2	2
ATB (min)	3.4	3.9	4.4	5.1
R.B (cm/min)	0.58	0.51	0.45	0.39

Tables (4): Flame speed of Epoxy with carbon fiber in different ratio

additives	Epoxy	5%C.F	10%C.F	15%C.F
AEB (cm)	2	2	2	2
ATB (min)	3.3	4.1	5.3	6.2
R.B (cm/min)	0.58	0.48	0.38	0.32

When used CNT the smoke density data is different and that appear in Fig (4), low-smoke, and self-extinguishing epoxy resin system when used CNT Multi-wall carbon nanotubes are highly effective flame retardants and that appear in values of smoke density rating ; they can also be more effective than fibers. Carbon nanotubes are candidates as flame retardant additives because of their highly elongated shape (high aspect ratio)[16].

Tables (5): smoke density data of Epoxy with CNT in different ratio

additives	Epoxy	0.001CNT	0.05%CNT	0.1%CNT
total smoke density (mm ²)	8010	2790	1440	1410
maximum smoke density	62	55	38	31
Smoke density rating (mm)	50.1	17.4	10.2	8.82

However, carbon nanotubes are organophilic and can be dispersed directly into the polymer. Even smaller amount of carbon nanotubes (0.5 wt%) can greatly reduce the smoke density rating and reduce the rate of burning during combustion. Moreover, the addition of carbon nanotubes increased the time of burning that listed in tables (6)

Carbon nanotubes exist as a macromolecule of carbon, analogous to a sheet of graphite rolled into a cylinder. The chemical bonding between carbon atoms inside nanotubes is always of sp² type, the same as in graphite, and provides them unique strength. Moreover, they align themselves into ropes held together by the vander Waals force and can merge together under high pressure, trading some sp² bonds to sp³ and producing very strong wires of nanometre lateral dimension. Due to the non-polar nature of original carbon nanotubes, they have good compatibility with many polyolefin including PP and PE. The application of carbon nanotubes in flame retarded polymer material was first discovered by Kashiwa of NIST in 2002 [16]. In the study of PP/multiwall carbon nanotube (MWNT) composites, they found that carbon nanotube has two practical advantages for dispersing in PP compared with dispersing clay or silica into polyolefin. However, carbon nanotubes are organophilic and can be dispersed directly into the polymer. Compared with polymer/clay Nano composites, even smaller amount of carbon nanotubes (0.5 wt%) can greatly reduce the heat release rate and mass loss rate during combustion. Generally, the single walled carbon nanotube is more effective on the reduction of flammability properties than multi-walled carbon nanotube[17]. Due to the combination of size, structure and topology, the nanotubes display remarkable features. In particular, the graphitic nature of the

nanotube lattice contributes to provide high conductivity, high strength and stiffness, chemical specificity and inertness, while the elasticity provide optimal electronic properties, therefore the dimensions of carbon nanotube also affect the flammability properties [18].

Tables (6): Flame speed of Epoxy with CNT in different ratio

additives	Epoxy	5%C.F	10%C.F	15%C.F
AEB (cm)	2	2	2	2
ATB (min)	3.4	4.5	6.2	6.9
R.B (cm/min)	0.58	0.44	0.32	0.29

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