

Lifetime estimation of epoxy based composite materials on irradiating with gamma radiation for shielding applications

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ABSTRACT

The extensive application of polymer composites in the ionizing radiation conditions leads to durability issues where performance for a long run under the radiation environment is related. For the products, such as space applications; it is expected to have about 20 to 30 years of durability. In the case of polymer composites, the reactive intermediates like free radicals present in the polymers are capable of initiating chemical reactions resulting in scission and cross-linking on irradiation. It may result in the failure of material under the application. In the current work, polymer composites are developed to withstand such chemical reactions prepared by using different fillers and stabilizers and carried out decomposition studies to predict the stability of developed materials under ionizing radiation conditions. The lifetime is estimated by studying decomposition kinetics. The lifetime estimated for all developed samples is found around 20 to 45 years at 50 °C which is desired for a device under the nuclear environment.

1. Introduction

1.1. Objective

The extensive application of composites in the ionizing environment leads to durability issues where performance for a long run under the radiation environment is related. For applications, such as space, in a radiation environment, it is expected to have about 20 to 30 years of durability. The present work intends to carry out decomposition studies [1–3] to predict the stability of developed composites prepared by using modified epoxy with different fillers and stabilizers. Details of the preparation of such composites with different stabilizers and fillers are given in the following sections. The results are used to estimate approximate lifetime by assessing the relative stabilities of these developed composites likely to be used under gamma radiation conditions.

1.2. Introduction

Product lifetime is the desired quality to be specified for newly developed polymer or composite materials, along with other quality

assurance. It is going to be even more important for situations where onsite inspection is not feasible or chances of failure during the severe operating conditions. Traditionally for such products, based on the previous experiments and experience, life expectancy is used to predict. Understanding failure mechanisms at the micro-level and predicting long term performance or use under critical applications require a far better understanding of failure mechanisms to predict the life of the material using decomposition conditions. This method is useful for reliable lifetime predictions to be made.

Various types of radiations like x-rays, gamma rays, neutrons, alpha particles, and beta particles are ionizing radiations. On irradiating such rays, free radical forms degrade the polymer. Free radicals generated by ionization are highly reactive and it results in scission as well as cross-linking reactions. Free radicals, which are present in the material after irradiation, are responsible for changes in properties for a long time after exposure [4,5]. Near the earth's surface, the intensity of the radiation waves is not very high due to which polymer behavior may not change significantly. Hence radiation exposure tests are required only in applications where high radiation sources are in use, like nuclear plants; space applications; defense applications, etc [6].

Looking at the above conditions it is critically important to

Abbreviations: HALS, Hindered amine Light stabilizer; UV, Ultra Violet; TVP, Trivalent Phosphate; BNNP, Boron nitrided nanopowder.

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predicting the changes in polymer properties by modeling. However, modeling of kinetics of polymer degradation is quite complex and difficult to understand as the single rate expression of changes may not be valid over the long term service life. To understand failure mechanisms, it is necessary to design the test model for time-related degradation of polymers, and for that, it is important to know the composition, structure, chemical changes, and end product stresses [7].

The radiation hardened materials which are specially developed to use in the nuclear environment, for space application, a more accurate life expectancy is desired. In this study decomposition kinetic method is used for lifetime estimation of developed material testing only. However, the components must be tested for high-energy heavy-ion irradiation for accurate lifetime prediction.

1.3. Material selection

The polymers are widely used in electronics applications due to their ease of achieving desired properties by manipulating polymer structure and formulations. Also, ease of processing of polymers to convert them in finished articles with lower fabrication and manufacturing cost, compared to metals & ceramics, and the most important advantage of polymer is its lightweight with high strength have increased acceptability in industrial applications [8].

1.3.1. Epoxy

Epoxy resin is widely used in the encapsulation of electrical equipment and electronic devices. While molding the resin, due care should be taken, so that the flow of resin does not damage or displace the component [9]. As the molding of epoxy is a cold process, it does not damage the circuit and soldering of the component. Hence epoxy resin is chosen and it is modified with various fillers and stabilizers to compare their performance as a radiation-hardened shield.

1.3.2. Stabilizers

In general, hard glassy polymers that crosslink are more resistant to radiation damage than soft or flexible polymers. It is to be noted that, in the presence of air, oxygen reacts strongly with polymer chains, which generate oxygenated species, discoloration, and molecular weight degradation. These phenomena can be inhibited or slow down by modifying polymers using suitable stabilizers.

In this study combinations of stabilizers were used. HALS was chosen as a primary stabilizer & UV Absorber and TVP were chosen as secondary stabilizers. HALS absorbs UV radiation, and inhibit degradation of the polymer. It slows down the photochemically initiated degradation reactions to some extent, in a similar way to antioxidants [10,11].

The UV absorber 2-(2'-hydroxy-3',5'-dipentyl-phenyl) benzotriazole are an effective stabilizer for γ -ray-induced degradation. UV Absorbers effectively inhibit the formation of alkyl free radicals under γ -irradiation and it is possibly the fundamental reason for its high stabilizing efficiency [12].

Organic phosphites combined with HALS [13] were used as stabilizers. A strong synergistic effect may be observed for the molecule with HALS and phosphite.

The efficiency of the mixture depends upon the chemical structure of the phosphite and HALS structural units as well as on the ratio of the components.

1.3.3. Fillers

Composites are engineering materials made up from two or more constituents with considerably different physical or chemical properties which remain separate and individual on a macro level within the finished structure. Most composites are made up of two materials. The material (the matrix or binder) surrounds and binds together a cluster of fibers or fragments of a much stronger material (the reinforcement). For the matrix, composites use thermosetting or thermoplastic polymers (also called resins). The resin hold the reinforcement together and help

to determine the physical properties of the end product.

In this study, epoxy resin has been selected because of its good mechanical, thermal, and corrosion resistance properties. Different composites were prepared using Graphite [14], Lead [15], and Boron Nitrided nano powder [16] as fillers.

2. Experimental

2.1. Specimen preparation

2.1.1. Eight compositions were prepared using different fillers and a combination of primary and secondary stabilizers

(i) Pure epoxy resin (ii) Epoxy + HALS + UV absorbers (iii) Epoxy + HALS + TVP (iv) Epoxy + Graphite Powder + HALS + UV absorbers (v) Epoxy + Graphite Powder + HALS + TVP (vi) Epoxy + Lead Powder + HALS + UV absorbers (vii) Epoxy + Lead Powder + HALS + TVP (viii) Epoxy + boron nitrided nano powder (BNNP) + HALS + TVP. Now onwards above samples will be designated as sample no. 1 to 8 in the whole document.

Commercial-grade Epoxy resin with a density of 1.12 g/cm³ with 15 P viscosity at 25 °C was used. Specimens were cast into our own designed steel frame. The sheets of 300 mm × 300 mm X 3 mm size were prepared and the samples of size, 150 mm × 50 mm x 3 mm cut for the irradiation experiments. Samples irradiated with different dose rates, i. e. 10 kGy, 20 kGy, 30 kGy, 40 kGy, 50 kGy. After irradiation, the same samples were tested for lifetime analysis using TGA [17].

2.2. Procedure

Samples were prepared using the gravity casting method. The gravity casting method is a technology used to mold the resin without applying pressure. With this method, it is possible to mold uniform casting of component resin with filler content [18,19].

In this research work graphite powder, lead powder, and boron nitrided nano powder were used as fillers. Bisphenol A based unmodified epoxy resin cured by hardener polyamide at room temperature used as the thermosetting matrix. The resin to hardener ratio of 2:1 was selected.

1 L (50 w %) Epoxy resin Stirred with very low speed (approx. 30 rpm) to avoid bubbles creation. Solution of 2% v/v primary (HALS) + 1% v/v secondary stabilizer (UV or TVP) and 3% w/v dry powder (filler) added into the resin mixture. Due care was taken to ensure uniform dispersion of fillers. Whole mixture was stirred under mild conditions, at 30 °C and created a homogeneous mixture. Hardener added into the mixture and stirred for 10 min, homogeneous mixture poured carefully into the frame to avoid any bubble generation/penetration inside the sheet during preparation. It as ensured to get uniformity in thickness. After 24 h, the sheet placed in hot air oven to post cure at 50 °C for another 24 h.

2.3. Irradiation of samples

Samples were exposed to gamma radiation for a different period of time in the Gamma chamber using ⁶⁰Co Source. After gamma exposure, the samples were characterized.

Gamma Chamber - 5000 is a compact self-shielded ⁶⁰Co gamma irradiator providing an irradiation volume of approximately 5000 cc. The samples were placed in an irradiation chamber located in the vertical drawer inside the lead flask.

The radiation field was provided by a set of stationary ⁶⁰Co sources placed in a cylindrical cage. The sources were doubly encapsulated in corrosion-resistant stainless steel pencils and tested with international standards. The lead shield provided around the source was adequate to keep the external radiation field well within permissible limits.

2.4. Lifetime estimation

The intention of these experiments was to predict the stability of developed materials under ionizing radiation conditions. In this study, the lifetime estimation is discussed for epoxy based various composite materials on irradiating with different doses of gamma radiation using standard methods.

2.4.1. Decomposition Kinetics methods for lifetime estimation [20]

It includes isothermal and constant heating rate methods. Requires a collection of multiple curves at multiple heating rates. The ultimate benefit obtained is in 'Life-Time' plots [21] (Graph.1).

2.4.1.1. Multiple heating rate method. Thermogravimetric Analysis (TGA) provides a method for accelerating the lifetime testing of polymers so that short term experiments can be used to predict in-use lifetime. Thermogravimetric Analysis (TGA), monitors weight changes in a material as temperature changes. In the TGA approach, the material heated at several different rates through its decomposition region. From the resultant thermal curves, the temperatures for a constant decomposition level are determined. The kinetic activation energy is then determined from a plot of the logarithm of the heating rate versus the reciprocal of the temperature of constant decomposition level. This activation energy may then be used to calculate the estimated lifetime at a given temperature or the maximum operating temperature. This TGA approach requires minimum three different heating profiles.

In this experiment, three TGA runs at different heating rates were selected. The TGA software generated prediction plots for Life Time Estimation on basis of the calculated activation energy & conversion.

2.4.2. Experiments for lifetime estimation

The specific experimental conditions used (such as temperature range and atmosphere), depend upon the material being tested. The sample weight was 40–60 mg. Decomposition profiles were obtained while heating at 5, 10, and 20 °C/min in a nitrogen atmosphere between 50 °C and 125 °C. The profile during the first 25% of sample weight loss was used for subsequent calculations.

2.4.2.1. Procedure to calculate results & estimate lifetime. The first step in the data analysis process is the choice of level of decomposition. A value of 5% decomposition level is a commonly selected for all samples.

The next step in the process was to calculate the activation energy (E) using the method developed by Flynn and Wall [22].

$$E = \frac{-R}{b} \left[\frac{d \log \beta}{d(1/T)} \right] \quad (1)$$

where:

- E = Activation Energy (J/mol)
- R = Gas Constant (8.314 J/mol K)
- T = Temperature at Constant Conversion (K)
- β = Heating Rate (°C/min)
- b = Constant (0.457)

The value for the constant b varies depending upon the value of E/RT. Thus, an iterative process was used where E is first estimated, a corresponding value for b was chosen, and then a new value for E was calculated. This process was continued until E no longer changed with successive iterations.

To calculate the estimated time to failure (t_f), the value of the temperature at the constant conversion point was first selected for a slow heating rate (β). This value, along with the activation energy (E) was used to calculate the quantity E/RT. Which was used to select a value for $\log P(X_f)$. $P(X_f)$ can then be calculated by taking the antilogarithm. The selection of a value for failure (or operation) temperature (T_f) used to

calculate the t_f from eq. (2).

$$\ln t_f = \frac{E}{RT_f} + \ln \left[\frac{E}{\beta R} \cdot P(X_f) \right] \quad (2)$$

$$T_f = \frac{E/R}{\ln t_f - \ln \left[\frac{E}{\beta R} \cdot P(X_f) \right]} \quad (3)$$

where:

- t_f = Estimated Time to Failure (min)
- E = Activation Energy (J/mol)
- T_f = Failure Temperature (K)
- R = Gas Constant (8.134 J/mol K)
- $P(X_f)$ = A function whose values depend on E at the failure temperature.
- β Heating Rate (°C/min)

eq. (3) may be used to calculate the maximum used temperature (T_f) for a given lifetime (t_f). Based on this calculations, graphs are generated for all samples. The exponential graph is plotted using temperature 50 °C, 75 °C, 100 °C, 125 °C. Refer Graph 1.

2.4.3. Thermogravimetric analysis (TGA)

TGA analysis of all samples are carried out for each sample after irradiation. Results are tabulated based on onset of degradation temperature, % residue at the end of test. Based on this table, results are discussed (Refer Fig. 2).

The descending TGA thermal curve indicates a weight loss occurred. Onset temperature that denotes the temperature at which the weight loss begins. The end of the curve shows the residual mass left at the end of the test. Refer Table 3, the residual mass in sample 1, 2 & 3 is less than rest of the samples; this shows the evidence of filler content in samples 4 to 8.

3. Results and discussions

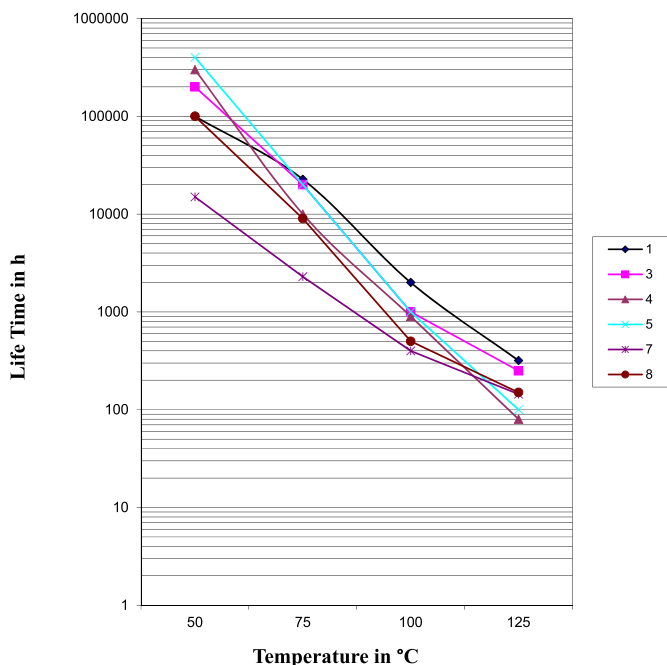
As per ASTM E1641: Standard Test Method for Decomposition Kinetics by Thermogravimetric analysis, the rate at which a kinetic process proceeds, depends not only on the temperature of the specimen is at, but also on the time it has spent at that temperature. The graph was plotted temperature v/s hours (Fig. 1) and detail results for each sample are discussed:

The lifetime of all the materials decreases with increase in temperature. At higher temperature, degradation of material becomes faster and lifetime decreases drastically that is expected for any such materials.

According to the graph shown in Fig. 1; the following points are observed:

A pure epoxy sample has 11 years of life expectancy. Sample no. 2 & 6 failed (decomposed) in the test on providing thermal stresses hence not considered in the graph. In other samples no. 1, 3, 4, 5, 7 & 8 have a good lifetime, which varies from 11 years to 45 years at 50 °C working temperature. On increasing temperature from 50 °C to 75 °C, the lifetime of all materials decreased. All samples with a stabilizer combination of HALS and TVP have given a good life expectancy. The best lifetime is found in Epoxy/Graphite/HALS/TVP (sample no.5). i. e. 45 years 50 °C (Refer Tables 1 and 2).

According to thermogravimetric analysis, Sample with lead filler shows very high residual mass than graphite and BNNP respectively. However, onset temperature for all samples are between 275 °C and 325 °C. All samples are thermally stable up to this temperature and total mass loss (100% decomposition) is found nearly 500 °C. Overall analysis says that the thermal stability is between 275 °C and 325 °C. Which is quite higher than the working temperature of electronics appliances. Even in space craft the working temperature of any electronics device is



Graph 1. Comparison of Life Time (in h) at different temperatures for developed materials.

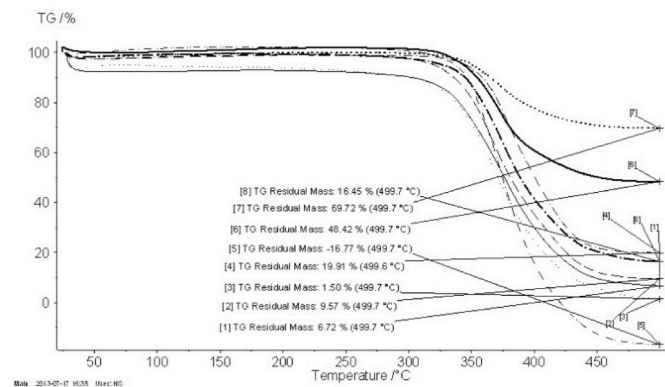


Fig. 2. TGA results of samples after irradiation.

Table 1
Comparison of Life Time (in h) at different temperatures for developed materials using Decomposition Kinetics methods.

Temp °C/ Sample No. °C	Life Time in h.					
	1	3	4	5	7	8
50	100000	200000	300000	400000	15000	100000
75	22700	20000	10000	20000	2290	9000
100	2000	1000	900	1000	399	500
125	318	250	80	100	144	150

considered nearly 50 °C (Refer Table 3).

4. Conclusion

Generally working temperature to be maintained for any electronic device is about 50 °C or less. As per the graph shown in Fig. 1, at 50 °C, the minimum lifetime for pure epoxy (Sample 1) is 11.4 years. Samples 3, 4 & 5 are beyond 11.4 years, sample 7 is 1.71 years and there is no change in sample 8 it is 11.4 years.

Table 2
Comparison of Life Time (in years) at different temperatures for developed materials using Decomposition Kinetics methods.

Temp °C/Sample No.	Life Time in Years					
	1	3	4	5	7	8
50	11.42	22.83	34.25	45.67	1.71	11.4
75	2.59	0.48	1.14	2.28	0.26	1.02
100	0.23	0.11	0.103	0.114	0.046	0.06
125	0.036	0.03	0.009	0.0114	0.02	0.017

Table 3
Results of TGA.

Sample No.	Onset of degradation Temperature	Residue at the end of the test
	°C	%
1	300	6.72
2	325	9.57
3	300	1.5
4	325	19.91
5	325	16.77
6	325	48.42
7	325	69.72
8	275	16.45

In all samples with a combination of the stabilizers HALS + TVP have given better results than a combination of stabilizers HALS + UV absorber. Sample No. 2 & 6 decomposed reaching before 60 °C giving below 1 h lifetime value and hence no life can be estimated. So this two samples are not considered. Both the samples were prepared using stabilisers HALS + UV absorber. This combination has not performed well for stabilizing the material against radiation.

However, with graphite, it withstood because of better crosslinking properties imparted by graphite filler. Same is found with sample 5. Hence it may be concluded that a combination of HALS and TVP and Graphite as a filler is better for ionizing stabilization and even for thermal stability of the material in the ionizing environment.

As per thermogravimetric analysis all the samples have withstood up to 325 °C which is quite high than application temperature.

Epoxy/Lead and Epoxy/Graphite composites with HALS + TVP may be the best combination to use as a radiation-hardened polymer for shielding application which may be used in the harsh nuclear environment.

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

CRediT authorship contribution statement

Mamta Saiyad: Conceptualization, Visualization, Writing - original draft, Investigation, Software, Validation. **N.M. Devashrayee:** Conceptualization, Visualization, Data curation, Supervision, Writing - review & editing, Methodology.

Declaration of competing interest

No Conflict of interest.
Note: Please provide if there is any draft to submit conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2020.106929>.

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