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The influence of stabilisers on resistance to gamma radiation for epoxy based polymeric composite material

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ABSTRACT

In certain applications plastic materials are getting irradiated while in end use. High energy irradiation leads to the auto-oxidation and degradation. The primary approach for stabilization against post irradiation degradation is to use appropriate stabilisers. In this research work, an experimental analysis of the effect of dose rate of gamma irradiation on epoxy resin based samples prepared by using combinations of primary and secondary stabilisers is presented. The chemistry, reaction mechanisms and morphology changes are studied and its effect on mechanical properties is observed. The results show an improvement of mechanical strength as dose increases, indicating cross-linking over oxidative degradation.

1. Introduction

1.1. Objective

The objective of present study is to develop a plastic material for VLSI package, which could be a Radiation Hardened. Considering the ambient in the space, the frequency of radiation is very high. Hence, it is tried to develop a material which could be prevented from microcracks and could prevent material from early failure and increase life time. Selection of right stabilisers or a right blend of stabiliser will give the best results to get inhibition or slow down the structural deterioration of polymer.

1.2. Literature review

To overcome the back door lack of polymer composite aircrafts and spacecrafts over a metallic parts, design of a new light weight shield particularly for aeronautic application is needed, particularly in high frequencies of radiation [1]. For this, it's necessary to choose right stabilisers against degradation due to irradiation alongwith proper resin and matrix parts in the composites.

The primary approach for stabilization against post irradiation degradation is to use Anti Oxidants (AO) and radical scavengers. The blends of stabilisers may be used to get best results for irradiated samples, consisting of a hindered phenol, antioxidants, secondary stabilisers and hindered amine light stabilisers [2].

Organic materials, both natural and synthetic, readily undergo reactions with oxygen. Important properties of polymers often change and mainly molecular weight of polymers gets reduced by oxidative degradation as a result they may lose mechanical properties, surface appearance and discoloration of plastic parts. Oxidation may occur at every stage of life cycle of polymer. These phenomena can be inhibited or slow down by modifying polymers using suitable stabilisers [3].

1.3. Selection criteria for stabilisers

Following points were considered during the selection of stabilisers in accordance with Polymer Radiation Chemistry: [4].

- Charged particles above the electron binding energy eject an electron from the atom, that results in ionization. Particles below the binding energy may form excited states that generate free radicals (unpaired electrons), and/or a number of other chemical species.
- Irradiation may lead to either: (a) cross linking (b) chain scission.
- Cross linking results in: decreased elongation, increased tensile strength, increased modulus.
- Chain scission results in: brittleness, fracturing, gas generation, and sometimes depolymerization back to a liquid state.

Abbreviations: Comp., composition; ^{60}Co, Cobalt 60; AO, Anti Oxidants; SEM, scanning electron microscope; DMA, dynamic mechanical analysis.

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- All polymers are at risk; dose and damage assessment are required.

In general, hard glassy polymers that is 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 to generate oxygenated species, discoloration, molecular weight degradation, and much lower limiting doses.

Hindered amine light stabilisers do not absorb UV radiation, but act to inhibit degradation of the polymer. They slow down the photochemically initiated degradation reactions, to some extent in a similar way to antioxidants [5,6].

The UV absorber 2-(2′-hydroxy-3′,5′-dipentyl-phenyl) benzotriazole shows excellent stabilizing effectiveness in the γ-ray-induced degradation. UV Absorber could effectively inhibit the formation of alkyl free radicals under γ-irradiation, and it is possibly the fundamental reason for its high stabilizing efficiency [7].

Organic phosphites combined with hindered amine light stabilizers (HALS) were used as stabilizers. A strong synergistic effect may observe for the molecule with HALS and phosphite. The efficiency of the mixture depends upon the chemical structure of generally, the mixture of HALS and phosphite exhibit synergistic, antagonistic or additive effects. the phosphite and HALS structural units as well as on the ratio of the components [8].

2. Experimental

2.1. Method

On the basis of literature review the specimen thickness was determined i.e. 3 mm. Performed research had a number of character because eight different fillers are applied. The study is discussed, only up to different blends of stabilisers applied.

A commercial-grade epoxy resin with a density of 1.12 g/cm^3 with 15 poise viscosity at 25 °C was used. And specimens were cast into our own designed steel frame. The sheets of 300 mm × 300 mm × 3 mm size were prepared and the samples cut for the irradiation experiments. Samples were prepared according to ASTM standard D 638 for the tensile tests. Also Mechanical strength tests were carried out on a universal testing machine, applying all the requirements of ASTM standard D 638 for the tensile tests. All tests were carried out at the room temperature [9].

The gamma irradiation process was carried out at the Bhabha Atomic Research center, Mumbai. This equipment operates with ^{60}Co sources.

According to the ASTM standards, D 638, five samples were required for each determination of mechanical strength. Therefore, six sets of samples, mainly, for three compositions, for five radiation doses and one without radiation, were exposed inside the irradiation chamber using five dose rates .

2.2. Materials

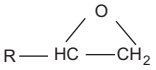
The thermosetting matrix used in this study was Bisphenol which a based unmodified epoxy resin cured at room temperature with 50% by weight of hardener. The density of the epoxy resin was 1.12 g/cm^3. Basic characteristics of stabilisers used are shown in Table 1.

2.3. Procedure

At the first stage, 400 ml of Epoxy resin is taken in a beaker and stirred with a very low rpm (Approximately 20–30 rpm). After this, stabilisers are diluted in suitable solvent and added into the resin drop wise. Stabilisers were taken in the ratio as shown in Table 1. The mixture is stirred slowly so that there is no formation of bubbles, however, continuous stirring is advisable. After adding hardener into the mixture, it is stirred for 10 min. to create homogeneous mixture. The curing time depends upon the amount of hardener added. Now the mixture is poured very slowly into the frame fabricated to get sheet of 300 mm × 300 mm × 3 mm. It was covered with toughened glass by applying releasing agent on it. It must be allowed to be cured for 6 h. The cured sheet is kept at room temperature for 8 h and then kept into the hot air oven for 24 h for post curing. The samples from different regions are cut using milling machine with suitable clamp of specified standard ASTM D638.

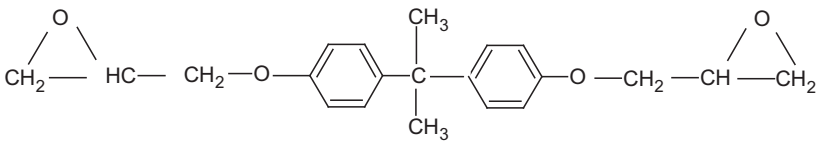
3. Chemistry

3.1. Chemistry of epoxy resin

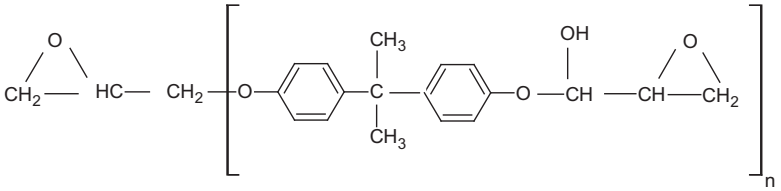
The term epoxy resin is applied to both the prepolymers and to cured resins, the former contain reactive groups,  (Epichlorohydrin), hence they are called as "epoxy" functionality [10].

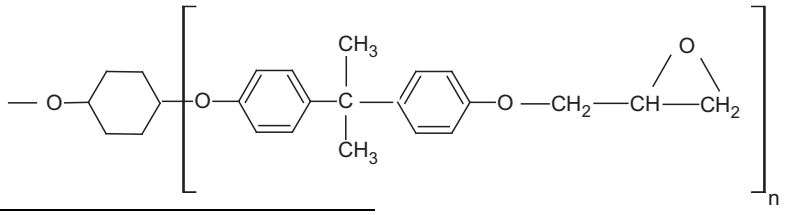
Liquid epoxy resins are converted through these reactive epoxy sites into tough, insoluble and infusible solids.

The simplest epoxy resin derived from the reaction of bisphenol A and epichlorohydrin is (2,2 – bis[4-(2′3′epoxy propoxy)phenyl]propane) commonly called diglycidyl ether of bisphenol A.



The higher homologs are represented by the following theoretical structure.



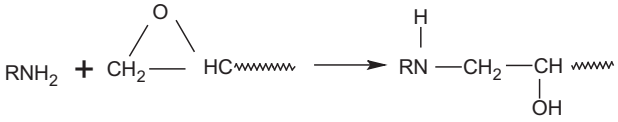


With increasing molecular weight, another reactive site – OH – group was introduced. This group can react at higher temperature to give additional cross linking. Lower value of '*n*' gives shorter length of chain.

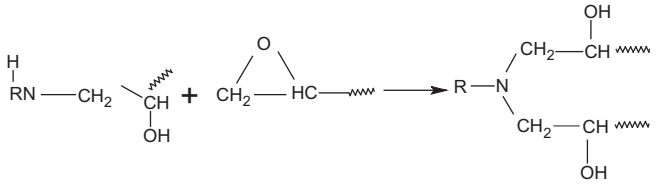
3.2. Chemistry of epoxy on adding hardener

Here, Polyamine is used as reactive cross-linking agent for liquid epoxy resin.

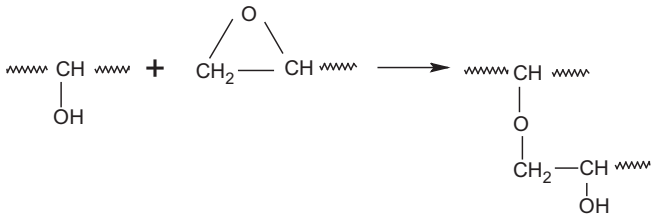
The amine reacts with the epoxy group through active amine hydrogen. Each primary amine group is theoretically capable of reacting with two epoxide groups and each secondary amine is capable of reacting with one group of epoxide; reaction is as follow:



The secondary amine thus formed reacts further;



Theoretically, the hydroxyls formed is capable of reacting with epoxy groups to form ether linkages.



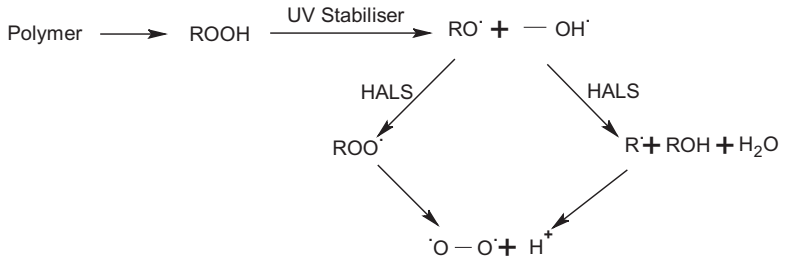
This reaction is often catalysed by tertiary amines. However, the tertiary amine formed by the epoxy secondary amine reaction is apparently too immobile and sterically hindered to act as a catalyst.

Here, the proportion of resin to hardener used is 2:1 as epoxy resins are blended, filled or modified with reactive and nonreactive components. Hence, it's necessary to adjust concentration of the curing agent to resin and reactive components [11].

3.3. Reaction mechanism after adding stabilisers

The primary stabilisers are used to retain the original molecular structure of the polymer under the effect of Light, Heat or radiation and secondary stabilisers are generally used to provide additional attribute to the polymer for value addition at the end use of polymer. Primary antioxidants are generally radical scavengers or H-Donors. Here two different combinations of primary and secondary stabilisers are used for epoxy resin to be stabilized against gamma radiation. The combinations are shown in Table 1. The combine effect may be explained by following mechanism;

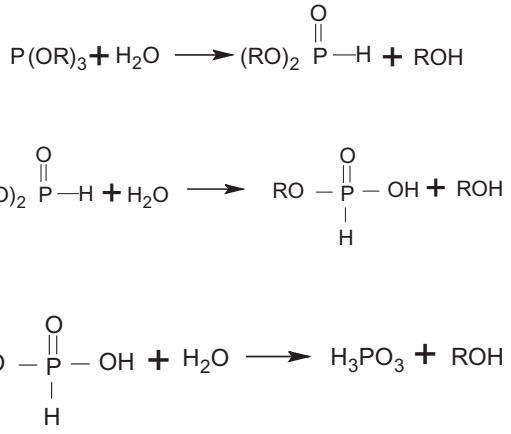
3.3.1. Combination 1

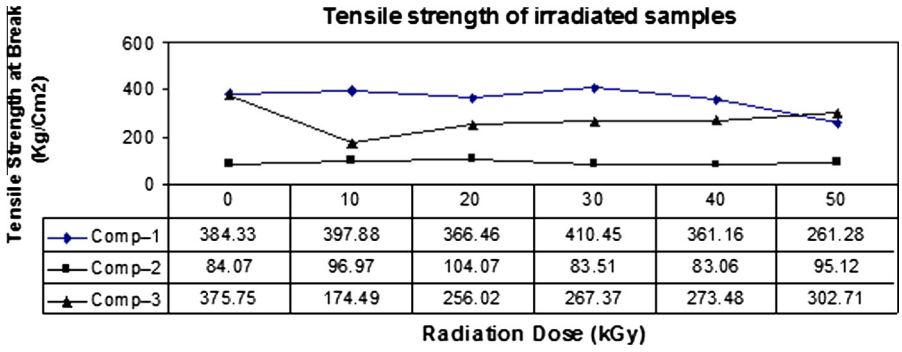


$$ROO^{\circ} + R^{\circ} + ROH + H_2O \rightarrow [RO^{\circ} + OH] + [RO + OH] + H^{+}$$

3.3.2. Combination 2

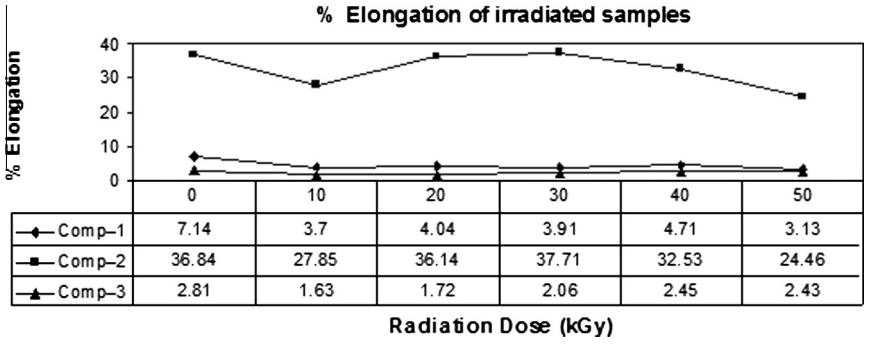
Secondary antioxidants are typically hydroperoxide decomposers, such as trivalent phosphorous compounds:





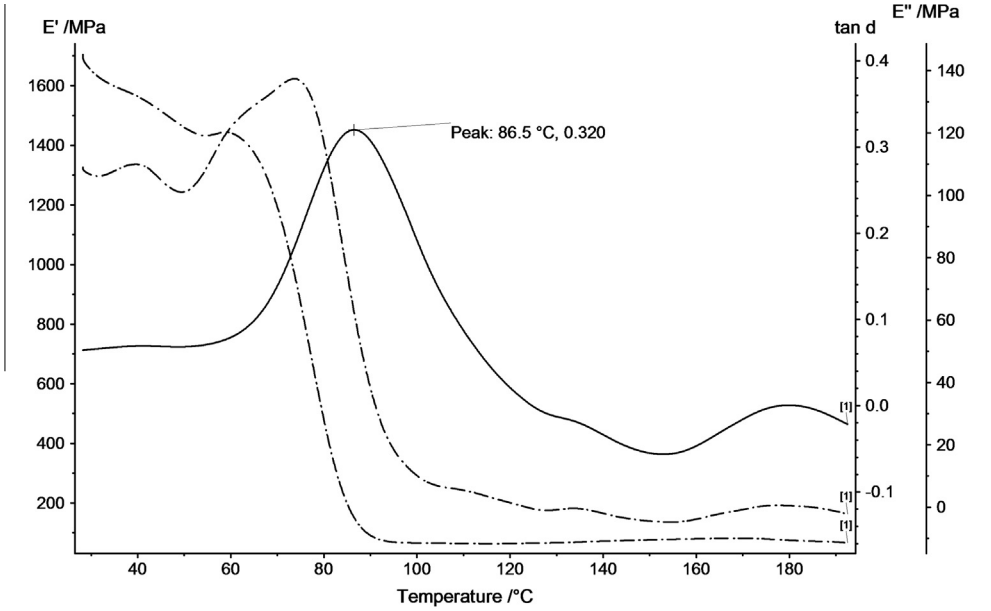
	0	10	20	30	40	50
Comp–1	384.33	397.88	366.46	410.45	361.16	261.28
Comp–2	84.07	96.97	104.07	83.51	83.06	95.12
Comp–3	375.75	174.49	256.02	267.37	273.48	302.71

Graph 1.

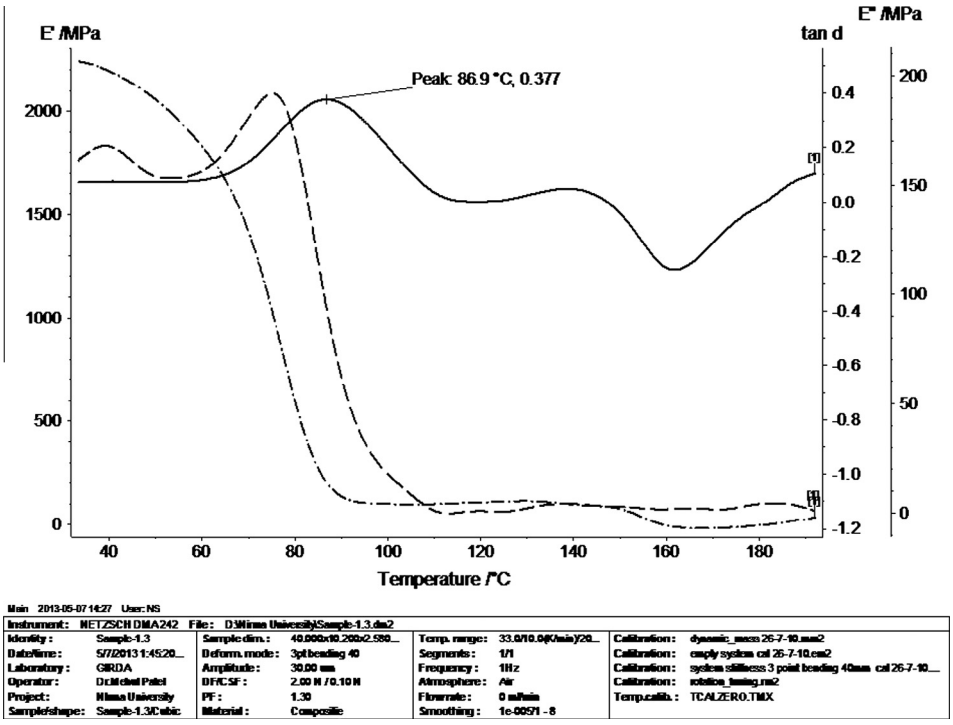


	0	10	20	30	40	50
Comp–1	7.14	3.7	4.04	3.91	4.71	3.13
Comp–2	36.84	27.85	36.14	37.71	32.53	24.46
Comp–3	2.81	1.63	1.72	2.06	2.45	2.43

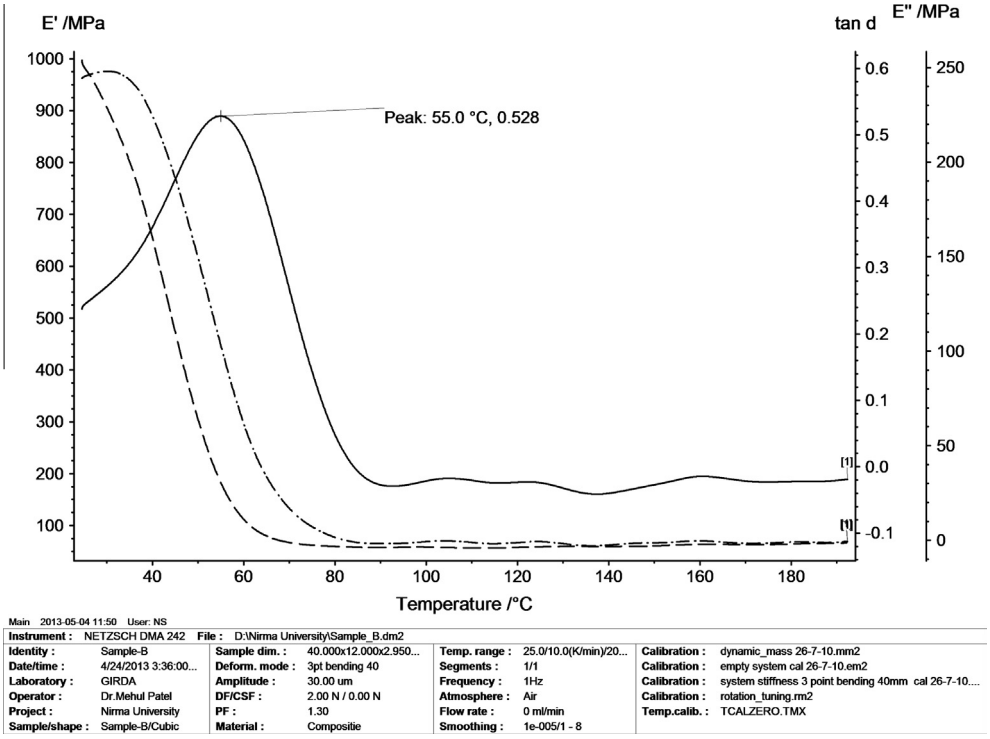
Graph 2.



Graph 3.1. Non irradiated - composition 1



Graph 3.2. Irradiated - Composition 1



Graph 3.3. Non irradiated - Composition 2

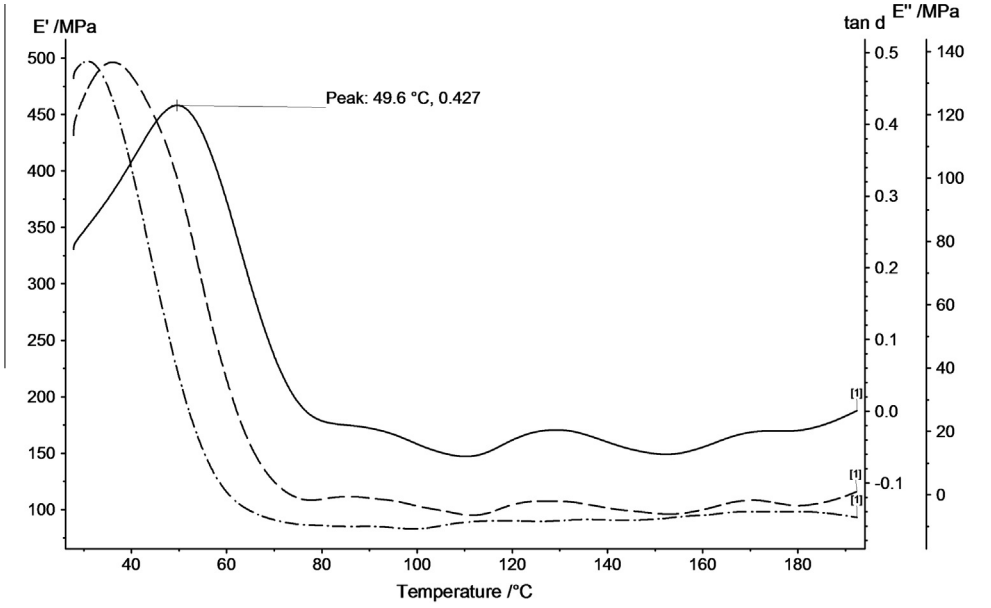
Above process of stabilization protects polymer against decomposition during irradiation.

4. Results and discussion

4.1. Mechanical properties

Mechanical properties of the samples was taken as a basis of comparison for different compositions and different doses of gamma irradiation. Mainly Tensile strength at Break and % Elongation were compared to establish the properties changes.

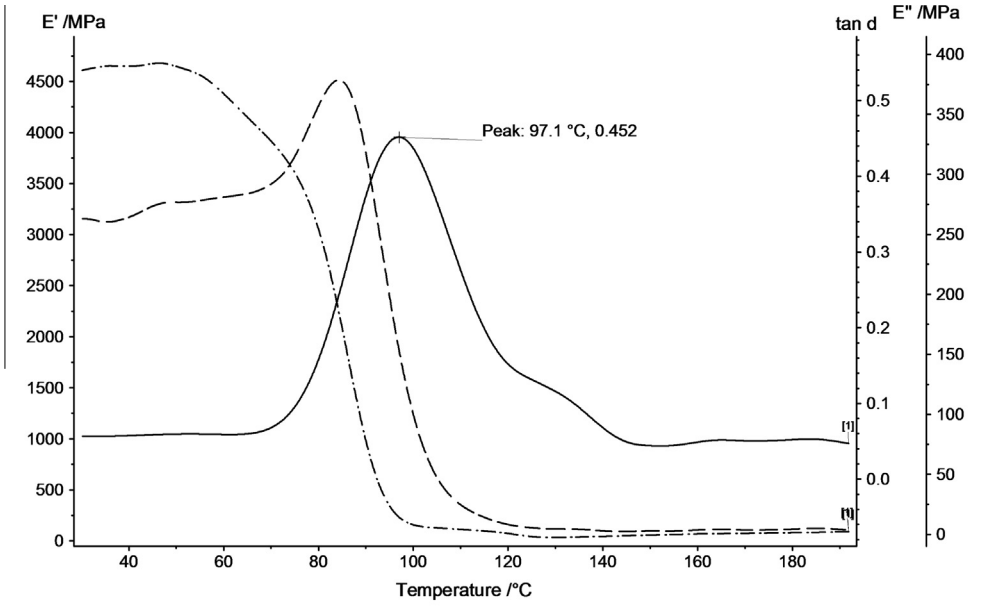
Comp. 1 – Without using any stabilisers.
Comp. 2 – Combination of HALS and UV absorbers.
Comp. 3 – Combination of HALS and phenolic antioxidants.



Main 2013-05-04 11:41 User: NS

Instrument :	NETZSCH DMA 242	**File :**	D:\Nirma University\Sample-2.2_26-04-2013.dm2				
Identity :	Sample-2.2	**Sample dim. :**	40.000x9.500x2.650...	**Temp. range :**	28.0/10.0(K/min)/20...	**Calibration :**	dynamic_mass 26-7-10.mm2
Date/time :	4/26/2013 11:18:40...	**Deform. mode :**	3pt bending 40	**Segments :**	1/1	**Calibration :**	empty system cal 26-7-10.em2
Laboratory :	GIRDA	**Amplitude :**	30.00 um	**Frequency :**	1Hz	**Calibration :**	system stiffness 3 point bending 40mm cal 26-7-10....
Operator :	Dr.Mehul Patel	**DF/CSF :**	2.00 N / 0.00 N	**Atmosphere :**	Air	**Calibration :**	rotation_tuning.rm2
Project :	Nirma University	**PF :**	1.30	**Flow rate :**	0 ml/min	**Temp.calib. :**	TCALZERO.TMX
Sample/shape :	Sample-2.2/Cubic	**Material :**	Compositie	**Smoothing :**	1e-005/1 - 8		

Graph 3.4. Irradiated - Composition 2



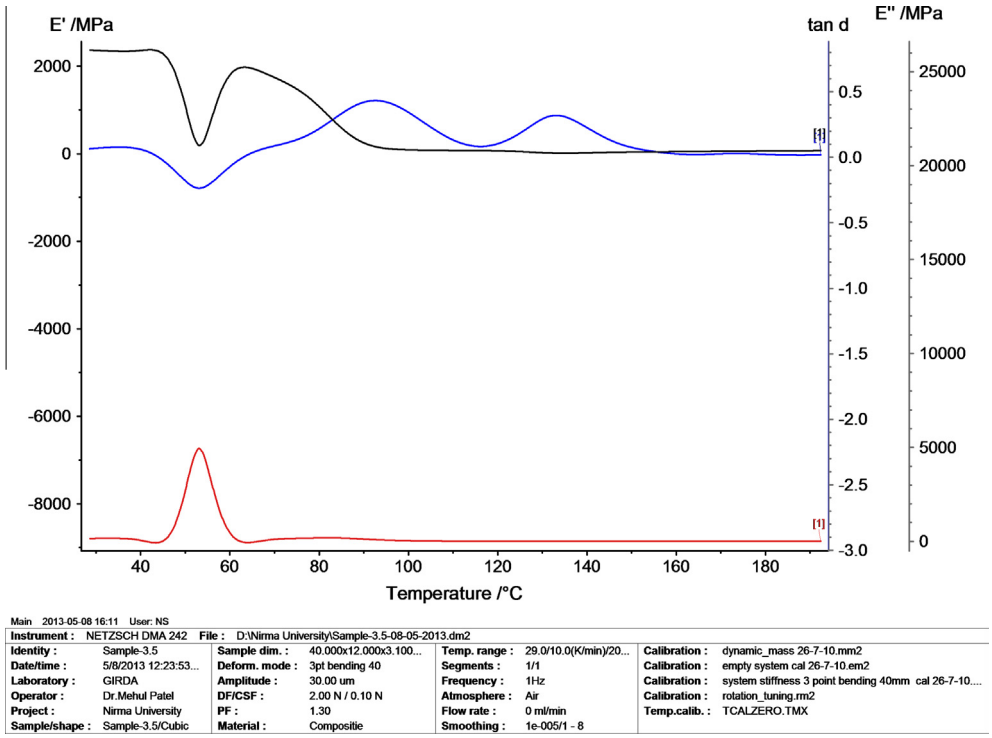
Main 2013-05-07 11:33 User: NS

Instrument :	NETZSCH DMA 242	**File :**	D:\Nirma University\Sample-C.dm2				
Identity :	Sample-C	**Sample dim. :**	40.000x12.000x3.000...	**Temp. range :**	31.0/10.0(K/min)/20...	**Calibration :**	dynamic_mass 26-7-10.mm2
Date/time :	5/7/2013 11:10:17...	**Deform. mode :**	3pt bending 40	**Segments :**	1/1	**Calibration :**	empty system cal 26-7-10.em2
Laboratory :	GIRDA	**Amplitude :**	30.00 um	**Frequency :**	1Hz	**Calibration :**	system stiffness 3 point bending 40mm cal 26-7-10....
Operator :	Dr.Mehul Patel	**DF/CSF :**	2.00 N / 0.10 N	**Atmosphere :**	air	**Calibration :**	rotation_tuning.rm2
Project :	Nirma University	**PF :**	1.30	**Flow rate :**	0 ml/min	**Temp.calib. :**	TCALZERO.TMX
Sample/shape :	Sample-C/Cubic	**Material :**	Compositie	**Smoothing :**	1e-005/1 - 8		

Graph 3.5. Non irradiated - composition 3

Value on X axis shows the doses rate starting from Zero which indicates non irradiated sample. 10–50 kGy gamma radiation dose rate using ^{60}Co.

The mechanical strength parameter values obtained from tensile strength at yield and % elongation for each dose rate. (i) The values of comp. 3 for tensile strength at yield are increased as absorbed dose increased and % elongation decreased drastically. No effect of dose rate on % Elongation is observed. This proves that the material has toughened and cross linked on irradiation. (ii) While in sample 2 the % elongation has increased on irradiation and tensile strength at yield decreased on irradiating samples, which infers the material has become flexible and chain



Graph 3.6. Irradiated - composition 3

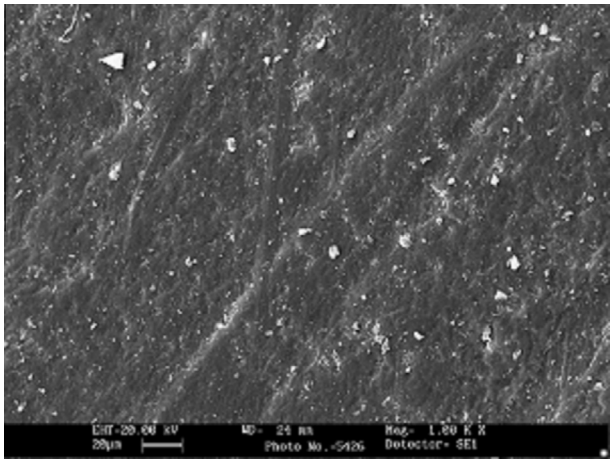


Image 1.1.

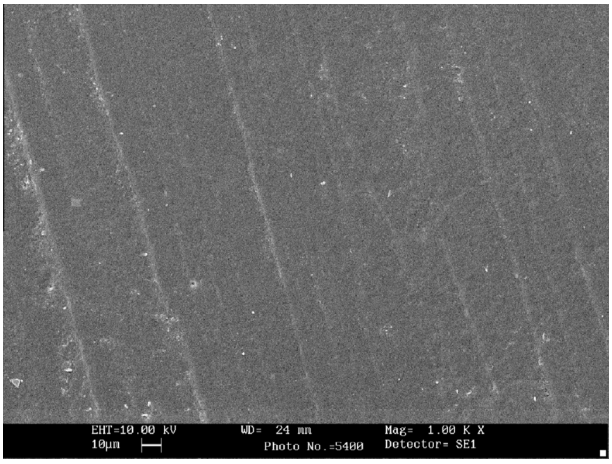


Image 2.1.

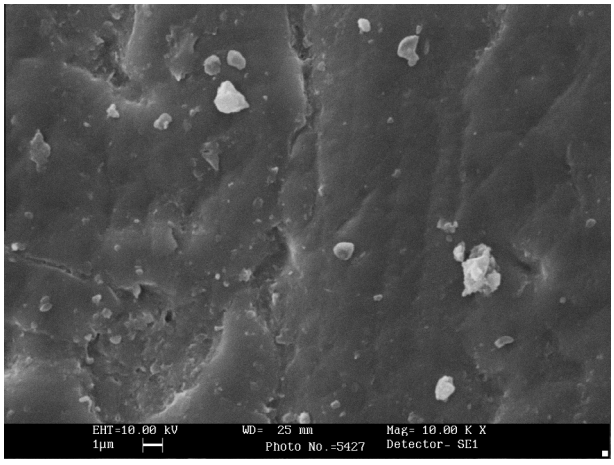


Image 1.2.

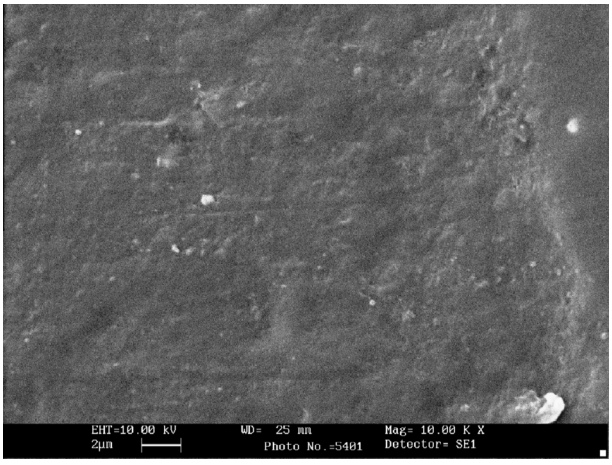


Image 2.2.

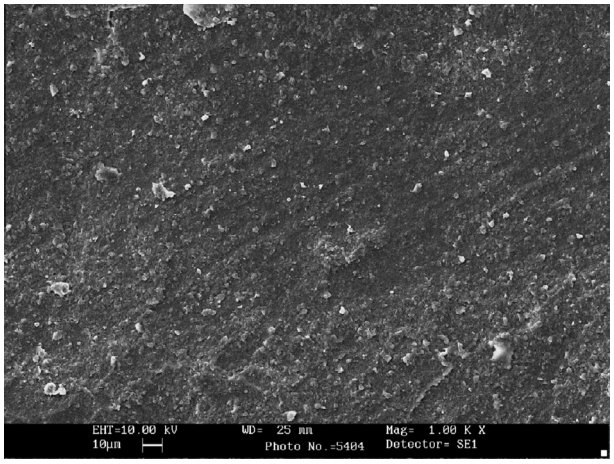


Image 3.1.

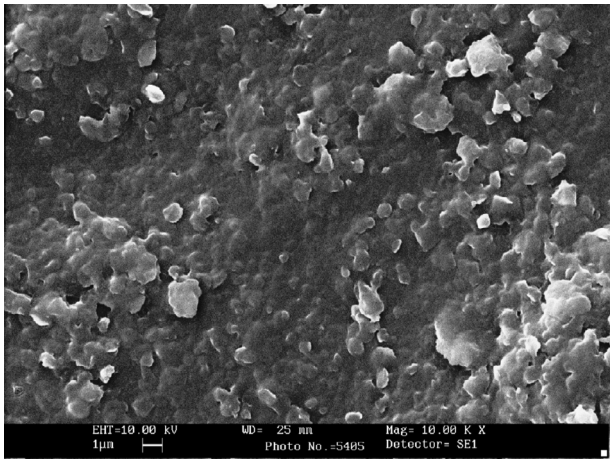


Image 3.2.

scission have occurred. (iii) Comp. 1 also shows cross linking in polymer chains. (iv) Most of the measured data are above the measured value for the nonirradiated sample of comp. 3. However, the large spread of the measured values makes it difficult to analyze the tendencies.

(v) An analysis of show that the yield stress for tensile tests was apparently more influenced by irradiation at lower dose rates and was fairly good on increasing the dose rate for comp. 3.

(vi) A possible explanation for this behavior could be that, in composition 3, at lower dose rates, oxidative degradation was predominant due to the slower consumption of the oxygen present in the samples. As dose rate increased, the oxygen was more rapidly consumed, and after the oxygen in the sample was totally consumed, the free radicals formed by irradiation began to improve cross-linking between molecules. (vii) The modulus of elasticity was found decreased over all dose rate intervals compared to non-irradiated samples. (viii) Despite the fact that irradiation was carried out in the presence of air, the improvement in epoxy resin mechanical strength properties for certain conditions show the predominance of cross-linking over oxidative degradation on using combination of stabilisers No. 3.

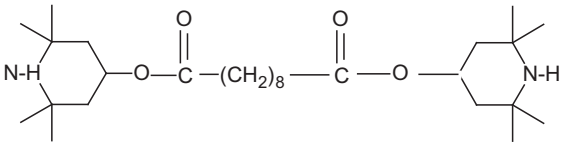
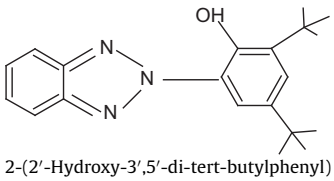
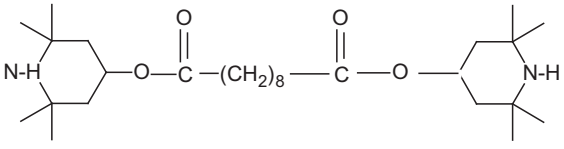
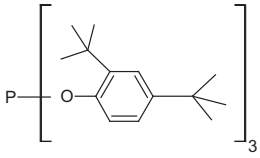
The difficulties experienced in analyzing trends in many of the measured parameters (for instance, yield stress and modulus of elasticity) can be associated with many factors. Firstly, there are experimental limitations and uncertainties related to the obtainment of the stress–strain curves and to the evaluation of the mechanical properties. Another possible factor is the nature of many reactions occurring simultaneously during irradiation that can produce opposite effects (see Images 2.1, 2.2, 3.1, and 3.2).

4.2. SEM analysis

SEM images were acquired on a Model LEO 440i at a chamber pressure of 50 Pa. 20 kV electron beam was employed for scanning of minimize any possible charging effect. The regions of low pixel intensity are attributed to regions composed of polymer resin. In first composition the morphology of the sample shows the granular nature of the sample with irregularity whereas, after the irradiation the surface is seems to be rough in nature. This is an evident derived from the tensile test results.

In the second composition, the sample without irradiation (See Image 1.1) shows a flat topography and after irradiation it displays large scale surface damage leading to considerable surface roughening.

Table 1
Basic characteristics of stabilisers used in experiments.

	Primary stabiliser	Secondary stabiliser
Combination 1		
	Hindered amine light stabiliser (HALS)	UV absorbers
Chemical structure		
IUPAC name	Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate	2-(2′-Hydroxy-3′,5′-di-tert-butylphenyl) benzotriozole
Ratio	2:1	
Combination 2		
	Hindered amine light stabiliser (HALS)	Phosphite anti oxidant
Chemical structure		
IUPAC name	Bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate	Tris(2,4-di-tertbutyl phenyl)phosphite
Ratio	2:1	

The polypoid contains topography after irradiation. Primarily the particle size was much smaller while non irradiated, and shows increase in particle swelling after irradiation (See Image 1.2).

4.3. Dynamic mechanical analysis (DMA)

The instrument used for DMA is DMA 242C of Netzch Germany. This test has helped in determining the effect of different curing conditions of thermoset Epoxy sample. It demonstrates the degree of cure based on the stiffness and glass transition temperature of the samples. Optimum cure is important to ensure that thermoset materials retain the required stiffness needed at the elevated temperatures.

In the above shown graph; the resultant sinusoidal strain is measured through the application of a variable sinusoidal stress to a sample. The relationship between complex modulus, storage modulus and loss modulus are often shown as a right angle triangle. The hypotenuse is complex modulus. The tangent of the phase angle equals the ratio loss modulus/storage modulus. Comparison of Tan δ is shown in the graph.

DMA comparison of all three samples are shown above, all non irradiated samples have almost similar deflection temperatures under load (DTUL), shown as a peak. However, the mechanical response below and above the DTUL of each is different (See Graph 3.1, 3.3 and 3.5). In irradiated samples, for composition 1 (See Graph 3.2) and composition 3 (See Graph 3.6), the deflection varies as shown by the more No. of peaks, which shows the samples are damaged due to radiation, but in sample 2 (See Graph 3.4) the peak has remained almost same as in non irradiated sample.

The test was carried out with 3 point bending deformation mode, Frequency: 1 Hz, in air.

5. Conclusion

Analysis of the changes in the mechanical properties of the Epoxy composite material submitted to gamma irradiation shows that (See Graphs 1 and 2) (i) there is a significant change is noted for combination 3. On irradiation, the cross linking has occurred which has increased the tensile strength at yield and decreased the modulus of elasticity. (ii) Whereas exactly opposite results are observed in case of combination 2. Tensile strength has decreased and % elongation has been increased. (iii) most of the values for the tensile tests were higher than those for the nonirradiated samples, although tendencies were not well identified; (iv) the modulus of elasticity for the tensile tests decreased over all dose and dose rate intervals. This effect was more pronounced at lower dose rates.

It is important to observe that the experimental framework used in this work was designed to allow a comparative study of the mechanical strength properties of two types of stabilisers blends for nonirradiated and irradiated samples of Epoxy material. Thus, the validity of the data and conclusion obtained are limited by the assumptions and material used.

Considering the experimental data from a comparative perspective, the results show an improvement in material with combination 2 mechanical strength properties as dose increases, indicating the predominance of cross-linking over oxidative degradation, despite the irradiation in air, which would theoretically ensure oxygen availability across the sample.

Considering the DMA data, the stability of material is better in combination 2. Hence we may conclude that combination of composition 2 gives more stability against gamma radiation even at 50 kGy dose rate.

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