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Thermo-mechanical characterization of carbon fiber composites with different epoxy resin systems

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ABSTRACT

The composite materials have found widespread applications in aircraft, automobiles, sports, space, and defence industries. Understanding the cure behavior as well as resulted thermo-mechanical properties of a thermosetting system are essential in the development and optimization of composite fabrication processes. In this paper, HCU200/A45 carbon fiber prepreg along with HinpoxyC, HinpoxyVB, ARL135 and ARL136 epoxy resin systems with suitable hardeners are used for the development of composites and their characterization. The DMA, isothermal and dynamic modes of DSC, Kissinger equation and the universal tensile test are used to determine various thermo-mechanical properties of composites namely glass transition temperature, heat of reaction, degree of cure, activation energy, pre-exponential factor and tensile strength. The simple additive weighting method is applied to compare different epoxy resin systems and it is found that the overall thermo-mechanical properties for ARL136 resin system are within 5% variation of the same properties measured for the prepreg system.

1. Introduction

A composite material is a combination of two or more chemically different materials on a macroscopic scale to get the best properties out of its constituents. There has been an increased interest in modeling of epoxy-based composite processing with the growth of computer-aided design and manufacturing [1]. For the use of composites in various fields of applications like space, automobile, sports and aerospace with varying requirements, the proportion of mixtures needs to be changed which demands characterization. The main objective of the characterization of epoxy-based composites is to obtain high-quality parts with greater consistency and to minimize the experimental work required to establish a cure cycle for new components. Carbon fibre prepregs are ready-made tapes composed of carbon fibre fabric impregnated with reactive epoxy resin [2]. Prepreg materials are generally pre-cured and have higher molecular weight in order to reduce the resin flow, which facilitates storage and processing. The prepregs are laid on the mould in various orientations and then cured for fabricating the composite structure. The curing, the most crucial stage in the composite manufacturing, is the process of hardening of the polymer material by the cross-linking of the polymer chains. During cross-linking at sufficiently high temperatures, the material changes from a liquid via a gel into a glass-like solid. The typical epoxy material contains unsaturated polyester and polyurethane as a resin system and amines, anhydrides or peroxides as a hardener [3].

The glass transition temperature (T_g) is important in the characterization of the mechanical properties of thermoset polymers. It constitutes a parameter of high interest in the study of amorphous regions within semi-crystalline materials [4–6] and can be evaluated by several techniques and methods. The materials having ultra-low glass transition temperature cannot be directly measured by any instruments which can be obtained by polymer blending [7]. The degree of cure indicates the extent up to which a material is cured. The change in the enthalpy of a chemical reaction and whether the energy is released or absorbed during the reaction is judged by the heat of reaction. Activation energy is the minimum amount of energy that is required to initiate a chemical reaction. Pre-exponential factor decides how often the molecules collide with each other.

Different thermo-analytical methods like dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) are used to characterize epoxy resin systems, optimize manufacturing parameters and monitor the curing process of thermoset polymers [8,9]. These

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methods, however, typically are not practiced for in-situ cure monitoring, but are only performed in laboratories under ideal conditions [10]. DMA measures the change of complex modulus, which can be divided into the storage and the loss modulus, as a function of temperature [11,12]. Therefore, it is a useful method to observe changes caused by melting and cross-linking. The glass transition temperature, modulus information, curing behavior, etc. can be determined using DMA testing. The characterization of thermoset matrices for polymer composites requires the development of cure kinetic models to describe the state of cure within the polymer after the composite system has been subjected to a thermal history [13]. According to the International Confederation for Thermal Analysis and Calorimetry (ICTAC), DSC is a technique in which the heat flow rate to the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed [14]. DSC evaluates the change of temperature difference between a sample crucible and a reference crucible during a temperature ramp [8,14]. It can detect melting, evaporation, glass transition and also reactions by the consumption or release of heat [15]. The advantages of DSC are that only a small amount of the substance is needed as well as it can also provide results for the glass transition and the degree of cure in a single measurement. DMA methods are usually favoured to detect the glass transition temperature, often with a higher resolution due to the significant changes in mechanical parameters [4,9,12,16]. The activation energies for the prepreg and epoxy resin systems can be determined by DSC using Kissinger's method. The combined results of DSC and DMA techniques provide an in-depth characterization of the material thermal properties [17]. The standard universal tensile test is used to determine the mechanical tensile strength for each system.

Many researchers have determined various mechanical, chemical and thermo-mechanical properties of different prepreg and epoxy resin systems using various methodologies. Stark et al. [3] determined the correlation between actual glass transition temperature, degree of cure and curing time for HexPly 6376 carbon fibre prepreg using the temperature-modulated differential scanning calorimetry (TMDSC) method. Gracia-Fernández et al. [18] measured the dynamic glass transition temperature using both DMA and TMDSC with the same frequency and temperature profiles and found a correlation by choosing the phase angle as a response parameter using quasi-isothermal conditions. Kim et al. [19] developed a cure kinetic model and also determined the heat of reaction and glass transition temperature of the prepreg using both isothermal and dynamic DSC scans. The heat of reaction goes on decreasing with an increasing heating rate for AS4/3501-6, a carbon fiber reinforced epoxy resin. Sbirrazzuoli et al. [20] and Vyazovkin et al. [21] utilized DSC to investigate the cure kinetics under isothermal as well as dynamic conditions for diglycidyl ether of bisphenol A with mphenylenediamine and epoxynovolac resin systems. The experimental data proposed that a degree of cure increases, the activation energy decreases. Flammersheim and Opfermann [22] also examined the cure kinetics under isothermal and dynamic conditions for the same materials and found that in order to get a good model from the dynamic DSC measurements, at least three heating rates should be used and there should be at least one order of magnitude in the difference between the maximum and minimum heating rates. Kessler and White [23] developed a phenomenological cure kinetics model from dynamic DSC data of dicyclopentadiene cured with Grubbs' catalyst over a range of catalyst concentrations. The activation energy and pre-exponential factor were calculated using DSC at different heating rates, from 2 to 15 °C/min. Costa et al. [24] used DSC, DMA, and rheological techniques to investigate some of the kinetic parameters of cure reactions of a recent 8552-epoxy resin modified with thermoplastic, impregnated into carbon reinforcement, and to evaluate the curing cycle used to manufacture polymeric composites for aeronautical applications. Lee et al. [25] measured the heat of reaction, the degree of cure, and the viscosity of Hercules 3501-6 resin. Kwon et al. [26] evaluated interfacial and wetting properties of carbon fiber reinforced epoxy composites with different hardeners. Kim and Lee [27] developed a relationship between the dissipation factor and the degree of cure for carbon fiber epoxy materials. Kalogiannakis et al. [28] measured the thermal properties of carbon-epoxy and glass-epoxy used for the aircraft industries using modulated temperature DSC. The simple additive weighting (SAW) is the easiest multi-criteria decision making method for selection of the best alternatives. Akhmetova and Chichirova [29] proposed a technique for evaluating the reliability of heat-supply organizations with the use of the SAW method. Velasquez and Hester [30] provided a clear guide for how multi-criteria decision making methods should be used in particular situations. The SAW has vast applications in water management, business, and financial management.

In this paper, a carbon fiber prepreg tape along with four different epoxy resin systems have been considered to understand the cure behaviour and also to determine thermo-mechanical properties. The glass transition temperature has been determined using the DMA technique as per ASTM D7028 standard [31]. The various cure kinetic parameters like heat of reaction, degree of cure, activation energy, and pre-exponential factor have been determined using DSC technique according to ASTM D3418 [32] and ISO 11357 [33] standards. The effect of time and temperature on the heat flow has also been studied using DSC to identify heat of reaction. The activation energy and pre-exponential factor have been determined based on a Kissinger equation. The tensile strength for all the systems has been determined using universal tensile test according to ASTM D638 standard [34]. The SAW technique has been applied for selection of an epoxy resin system which gives optimum thermo-mechanical properties. The developed understanding of cure behaviour and resulted thermo-mechanical properties could be used for the development and optimization of the fabrication process.

2. Experimental

2.1. Materials

The carbon/epoxy HCU200/A45 prepreg, supplied by Hindoostan Technical Fabrics, is a non-bleed toughened high-performance prepreg being used in the space applications and aircraft industries. This prepreg consists of A45 thermoplastic toughened epoxy matrix and the HCU200 unidirectional carbon fabric. The mechanical and physical properties of the carbon fibers and epoxy have been described in Table 1. The HCP200 plain carbon fabric along with the mixture of different epoxy resin materials like Hinpoxy C, Hinpoxy VB, ARL 135 and ARL 136 with corresponding hardeners Hinpoxy C, Hinpoxy VB, AH 334 and AH 126 have been considered as an alternate of prepreg. The properties for carbon fabric HCP200 is same as HCU200 except for its weaving pattern, whereas technical specifications for different epoxy systems considered in this study have been given in Table 2. Hinpoxy C resin is a bisphenol-A based liquid epoxy resin and Hinpoxy C hardener is a colorless, low viscosity, modified amine hardener. Hinpoxy VB Resin is a bisphenol-A based liquid epoxy resin and Hinpoxy VB Hardener is a colorless, moderate viscosity, modified amine hardener. Lapox® ARL-135 is a modified epoxy laminating resin designed for high-performance applications and AH-334 is a modified polyamine based hardener. Lapox® ARL-136 is a modified bisphenol-A based epoxy liquid

Table 1
Mechanical properties of carbon fiber and epoxy.

Properties	HCU 200 – Fibre	A45 – Epoxy Resin
Density (g/cm^3)	1.8	1.2
Filament Diameter (10^{-6} m)	7	–
Tensile Strength (MPa)	3450	48
Tensile Modulus (GPa)	230	2915
Elongation Percentage (%)	1.5	1.6
Filaments	12 K	–
GSM	200	–

Table 2
Technical specifications of epoxy resin and hardener systems.

Epoxy systems	Viscosity (MPa) @ 25 °C	Density (g/cm^3) @ 25 °C	Mixing ratio	Cure time (Hrs.) @ 25 °C
Hinpoxy C (Resin)	9000–12000	1.15–1.20	100:30	24
Hinpoxy C (Hardener)	< 50	0.94–0.95		
Hinpoxy VB (Resin)	22,000–30,000	1.20–1.25	100:35	24
Hinpoxy VB (Hardener)	< 50	0.94–0.95		
ARL 135 (Resin)	1000–1500	1.1–1.2	100:32	24 + 8(@ 70 °C)
AH 334 (Hardener)	50–150	0.98–1.04		
ARL 136 (Resin)	2500–4500	1.14–1.17	100:90	1(@ 100 °C) + 6 (@ 160 °C)
AH 126 (Hardener)	100–300	1.1–1.2		

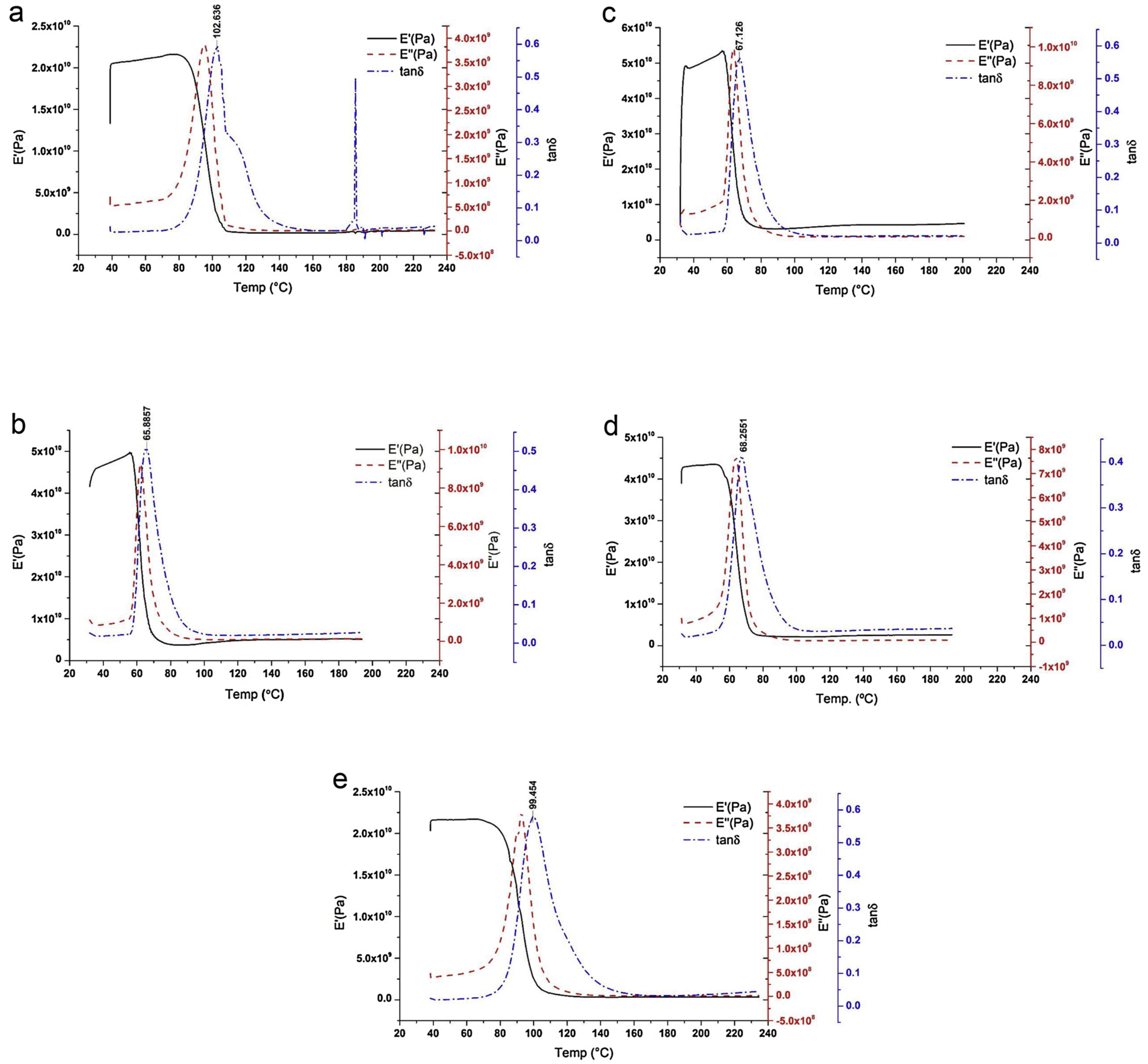

Fig. 1. a) Glass transition temperature for carbon fiber prepreg system. b) Glass transition temperature for Hinpoxy C epoxy resin system. c) Glass transition temperature for Hinpoxy VB Epoxy Resin System. d) Glass transition temperature for ARL 135 epoxy resin system. e) Glass transition temperature for ARL 136 epoxy resin system.

resin having a moderate viscosity and Lapox AH-126 is a liquid modified anhydride. The bisphenol-A epoxy resin is prepared from epoxidizing olefin with double bonds by hydrogen peroxide at low temperature. The bisphenol-A is used as an accelerator in the polymerisation process. The heat is generated while epoxy resin reacting with hardener due to the exothermic reaction. The cured epoxy resin has strong chemical stability because of the closed lock in the pile of dense structure, especially for solvent resistance.

2.2. Preparation of test coupons

In order to measure the glass transition temperature of prepreg and

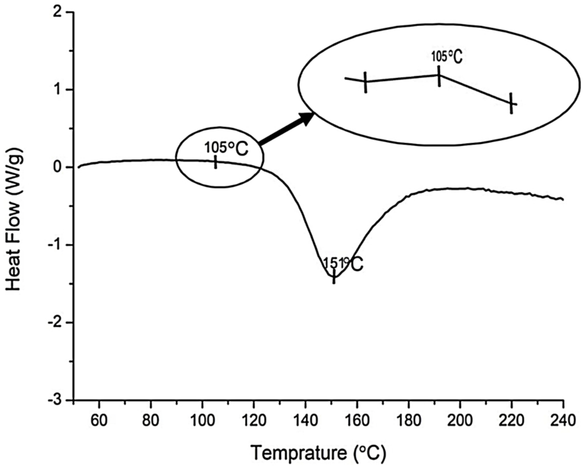

Fig. 2. Glass transition temperature for prepreg system obtained using dynamic DSC test.

Table 3
Glass transition temperatures for prepreg and epoxy resin systems using DMA and DSC tests.

Materials	Glass Transition Temperature (T_g) (in °C) using DMA test	Glass Transition Temperature (T_g) (in °C) using DSC test	% Difference
Prepreg	102.636	105	2.25
Hinpoxy C	65.8857	68.5	3.82
Hinpoxy VB	67.126	69	2.72
ARL 135	68.255	70	2.49
ARL 136	99.4547	103	3.44

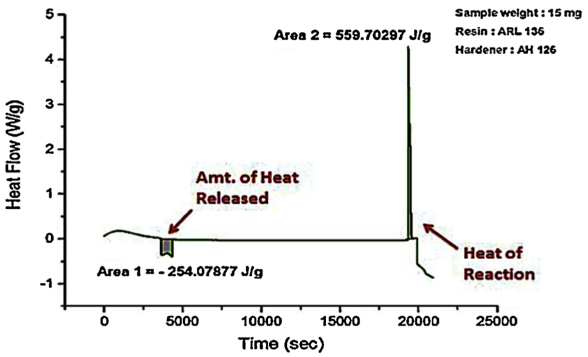

Fig. 3. DSC plot for heat flow v/s time for ARL 136 epoxy resin system.

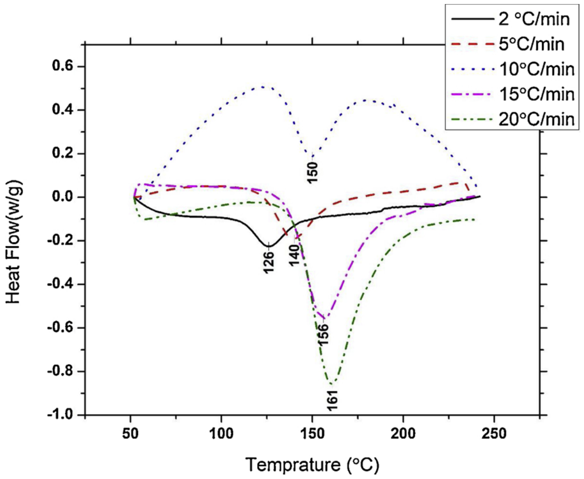

Fig. 4. DSC analysis at five different heating rates from 50 °C to 240 °C.

Table 4
Analysed DSC test data at five heating rates for curve fitting.

Heating Rate, β (°C/min)	Peak Temp., T_p (K)	$1/T_p$	$\ln(\beta/T_p^2)$
2	399.15	0.0025053	−11.2855
5	413.15	0.0024204	−10.4382
10	423.15	0.0023632	−9.7929
15	429.15	0.0023302	−9.4155
20	434.15	0.0023036	−9.1510

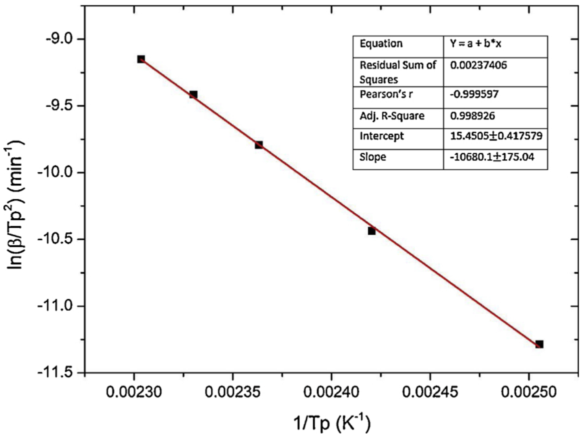

Fig. 5. Kissinger's plot to determine activation energy (E_a).

Table 5
Properties for prepreg and epoxy resin systems obtained using DSC test.

Materials	Heat of reaction (J/g)	Degree of cure	Activation energy (kJ/mol)	Pre-exponential factor (s^{-1})
Prepreg System	56.37208	0.48	86.7453	0.568×10^6
Hinpoxy C	212.5	0.26	90.9462	4.404×10^6
Hinpoxy VB	242.54	0.293	90.4523	3.245×10^6
ARL 135	538.4	0.383	89.7634	1.599×10^6
ARL 136	559.703	0.454	88.7944	0.913×10^6

different epoxy resin systems using DMA technique, coupons have been prepared in accordance with ASTM D7028 standard. The carbon fiber prepreg has been laid layer by layer on stainless steel mould with proper orientation. The prepreg layers along with consolidation materials have been cured in a hot air oven at 160 °C for about 3 h as per the curing cycle specified by prepreg manufacturer. The test coupons of size 56 × 12 × 3.2 mm have been cut from the cured sheet using a water jet cutting process. The resin and hardener have been mixed as per the mixing ratios given in Table 2. The carbon fiber sheets have been prepared from each epoxy resin system and layers of carbon fabric using the vacuum infusion process. The different curing cycles have been followed for different epoxy resin systems as suggested by the supplier. The test coupons of the same size have been cut from the cured sheet using a water jet cutting process.

The samples for DSC testing have been prepared from prepreg and epoxy resin systems as per ASTM D3418 and ISO 11357 standards respectively. The uncured prepreg having the weight of 5 mg have been used directly for DSC tests. The samples weighing approximately 15 mg have been prepared using different epoxy systems as per the mixing ratio shown against their names in Table 2.

The tensile strength test coupons have been prepared from the prepreg and the epoxy systems, according to the ASTM D638 standard. The same methodology has been followed to prepare test coupons for the tensile test as prepared for the DMA test. The overall size for test

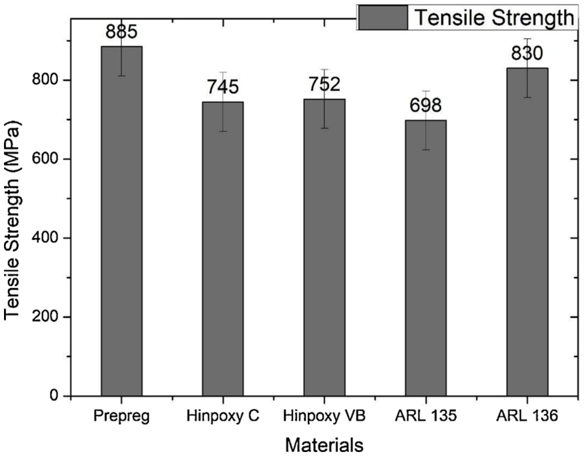

Fig. 6. Comparison of tensile strength of epoxy resin systems with prepreg.

coupons has been kept as 165 × 19 mm. The other dimensions of test coupons like gauge length, fillet radius, length and width of the narrow section have been considered as 50 ± 0.25 mm, 76 ± 1 mm, 57 ± 0.5 mm and 13 ± 0.5 mm respectively.

2.3. Testing procedure

DMA is a test method used to derive specific mechanical properties of the material as a function of temperature and frequency as well as to study the viscoelastic behavior of polymer. The highly sophisticated machine, EXSTAR make DMS6100 and calibrated using a metallic standard, has been used for the DMA test. The sinusoidal force at 1 Hz frequency has been applied to clamp mounted samples. The temperature of the sample has been controlled using thermoelectric heaters and at a same time corresponding strain has been measured by the Linear Variable Differential Transformer (LVDT). The response to the deformation can be monitored as a function of temperature or time. The equipment has been stabilized at 30 °C by 3 min before starting every experiment. The three-point bending clamping method has been selected for the DMA test because it is suitable for the stiffer materials like CFRP. Nitrogen has been used as a purge flow gas to prevent contamination during the curing process.

DSC method analyses the heat capacity of a material with respect to temperature and time. The PerkinElmer make TA DSC Q20 instrument along with Pyris software has been used for testing purpose. The uncured prepreg and different epoxy resin system samples, weighing approximately 5–15 mg, have been encapsulated in a standard sealed aluminium pan with a sealed lid. The encapsulated sample has been placed in a contained and controlled environment with the attachment of furnace and cooling rods. An empty aluminum sample pan and cover have been used as a reference during the test. The samples having known weight have been heated or cooled as quickly as possible and the corresponding change in the heat capacity of the material has been evaluated as a change in its heat flow. This helps to detect different transitions in the material such as glass transition, melting, change of phase, and its curing behaviour. The heat flow of crucible as compared to reference has been measured with the help of sensors mounted with thermocouples as a function of temperature and time. The DSC test uses a curing cycle in a controlled nitrogen atmosphere as an input. The cycle can either be based on the curing cycle of the resin system or standard cycle defined by the manufacturer of the DSC machine on the basis of a range of glass transition temperature of the samples. This cycle has been given in the form of commands which includes details of temperature, time and heating rate to be ensured for the desired test. The Pyris software has been used to operate the DSC test which can be controlled or ceased as and when necessary after setting up each component and parameter. The samples have been heated to 190 °C at 10 °C/min and held at 190 °C for 5 min to eliminate any thermal history. This test has been performed in two different ways: a) with the sample kept at constant temperature (isothermal scanning), and b) with the sample heated at a constant scanning rate (dynamic scanning). The isothermal DSC tests have been set for the temperature range of 50–240 °C with five different heating rates: 2, 5, 10, 15 and 20 °C/min.

The tensile strength for all the samples prepared using prepreg and different epoxy resin systems have been measured with the help of the universal testing machine. ADMET eXpert 1000 servo hydraulic testing machine has been used for tensile testing. The sample has been gripped using pneumatic vice in the machine and the proper amount of force has been applied during testing. The data acquisition system has been attached for generating stress-strain diagrams. The dedicated testing software provides the values of tensile strength, elongation, modulus of elasticity and poison's ratio of a test specimen. The multiple samples for the individual system have been tested to verify the accuracy of the obtained results.

3. Results and discussion

3.1. Measurement of glass transition temperature (T_g) for different epoxy resin systems

The glass transition temperature of carbon fiber prepreg and different epoxy systems have been determined using the DMA test and the same has been verified using DSC test. In the DMA test, stresses are generated in samples due to the application of sinusoidal forces. The strain has been developed within the samples after some phase shift (δ) as the material is not purely elastic. The value of stress amplitude (σ_A), strain amplitude (ε_A) and phase shift (δ) has been acquired for each sample. The storage modulus (*E'*), the material's ability to store the applied energy and the loss modulus (*E"*), the material's ability to dissipate energy that is applied to it have also been measured. The tan delta (tan δ), the ratio of the loss modulus to the storage modulus, has been used to evaluate the energy loss of materials from segment rearrangements and internal friction during the test. The samples have been heated from room temperature to 240 °C at a heating rate of 4 °C/min and the data, thus obtained has been used to check the effect of temperature on the modulus along with tan delta curve. The glass transition temperatures of the cured samples have been measured by

Table 6
The criteria for thermo-mechanical properties of different epoxy resin systems.

Properties Weighting	Glass transition temperature (°C) $w_j = 0.3$		Degree of cure $w_j = 0.4$		Tensile strength (MPa) $w_j = 0.3$		SAW value u_i	Rank
Materials	Original values	Normalised values	Original values	Normalised values	Original values	Normalised values		
Prepreg system	102.636	1	0.48	1	885	1	1	1
Hinpoxy C	65.886	0.642	0.26	0.542	745	0.842	0.662	5
Hinpoxy VB	67.126	0.654	0.293	0.610	752	0.850	0.695	4
ARL 135	68.255	0.665	0.383	0.798	698	0.789	0.755	3
ARL 136	99.455	0.969	0.454	0.946	830	0.938	0.951	2

taking the peak values of the tan delta curves obtained for each sample.

The effect of temperature on the modulus of materials has been presented in Fig. 1(a)–(e) for carbon fiber prepreg, Hinpoxy C, Hinpoxy VB, ARL 135 and ARL 136 epoxy resin systems respectively. It can be observed from the storage modulus curve (black full curve) that when the sample is in the glassy state, its storage modulus is very high and as the sample goes to the glass transition range due to an increase in temperature, storage modulus drops drastically this is because a lot of energy is consumed in the process of unlocking of the grains. Hence, at the same time, loss modulus rises during glass transition range as shown by the red dashed curve. The peak obtained by the tan delta curve (blue dash-dotted curve) gives the glass transition temperature (T_g) for corresponding systems. The sample exhibits rubber-like property after glass transition temperature is reached and can be plastically deformed.

The glass transition temperature for the prepreg as well as different epoxy resin systems have also been verified using the DSC test. The effect of temperature on heat flow for the prepreg has been shown in Fig. 2. The peak value has been observed at 151 °C, which indicates the crystallization temperature. The glass transition temperature (T_g) value has been taken from the intermediate point of transition which comes 105 °C. The similar procedure has been followed for all epoxy resin systems. The glass transition temperatures for different epoxy resin systems thus obtained have been given in Table 3. The percentage difference between the glass transition temperature obtained using both DMA and DSC tests for various materials is approximately 5%. The samples made from prepreg are having the highest glass transition temperature among all the selected materials. The samples made from ARL 136 epoxy resin are having higher T_g among other selected epoxy resin systems as well as almost 3% less compared to the prepreg system. This is because of mixing ratio of epoxy and hardener as well as a specific curing condition at elevated temperature. The difference of T_g within epoxy systems is approximately 30–35%.

3.2. Calculation of heat of reaction (H_R) and degree of cure (α)

The heat of reaction and degree of cure can be easily determined using DSC test. The heat flow in and out data with respect to time and temperature has been observed during DSC test. The heat of reaction is the change in the enthalpy of a chemical reaction that occurs at a constant pressure. The heat of reaction can be calculated by the Eq. (1).

$$H_R = \int_0^{t_f} (dQ/dt)dt \tag{1}$$

Where, t_f is the time required to complete the reaction.

The amount of heat released up to time t is determined by the Eq. (2).

$$H = \int_0^{t} (dQ/dt)dt \tag{2}$$

The effect of time on the heat flow has been plotted for each sample using data generated in DSC test. The data has been recorded for prepreg samples along with each epoxy resin sample during full curing cycle in isothermal and dynamic DSC mode from 50 °C to 240 °C at 10 °C/min. These graphs have two peaks, the area under the first peak gives heat released (H) whereas area under the exothermic peak i.e. the second peak gives heat of reaction (H_R). The degree of cure (α) is obtained by the ratio of heat released to heat of reaction (Eq. (3)).

$$\alpha = \frac{H}{H_R} \tag{3}$$

The effect of time on heat flow for the ARL 136 epoxy resin system has been plotted in Fig. 3. The area under first peak and area under second peak have been calculated as 254.07877 J/g in the isothermal DSC and 559.70297 J/g in dynamic DSC respectively. The degree of cure has been calculated as 0.45395 for this sample. The degree of cure is strongly affected by the cure temperature; a higher cure temperature accelerated the cure process in general.

The activation energies and pre-exponential factors for prepreg and epoxy systems have been calculated using Kissinger's method [35] based on the least square regression technique. DSC tests have been conducted in dynamic mode from 50 °C to 240 °C at five different heating rates, i.e., 2 °C/min, 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min. The effects of temperature on heat flow have been plotted for the DSC analysis at total five different heating rates as shown in Fig. 4 for the ARL 136 epoxy resin system. The peak temperature values from each curve are noted corresponding to its heating rate as described in Table 4. The peak temperature, T_p, shifts to a higher temperature range with increasing heating rate, β. Hence, the Kissinger method can be employed to calculate the activation energy and the pre-exponential factor of the cure of epoxy resin examined in this study.

A graph of $ln(\beta/T_p{}^2)$ versus $1/T_p$ has been plotted using the Eq. (4) [36], which is similar to the equation of a line. The fitted model is having R^2 value of 0.9989, which indicates that the model is a best fitted to a straight line. The slope of the linear fit graph and the Y-intercept value have been obtained from Fig. 5, to find the activation energy (E_a) and pre-exponential factor (A) respectively.

$$\mathrm{In}\left(\frac{\beta}{T_p^2}\right) = \mathrm{In}\left(\frac{AR}{E_a}\right) - \left(\frac{E_a}{R}\right)\frac{1}{T_p} \tag{4}$$

From Fig. 5, slope (m) = −10680.1, Y-intercept (c) = 15.4505.

Comparing Eq. (4), with $y = mx + c$, $m = -\frac{E_a}{R}$ & $c = ln\frac{AR}{E_a}$

So, the activation energy $E_a = -mR = 88794.35$ J/mol = 88.7944 kJ/mol (R = universal gas constant = 8.314 J/mol K)

The pre-exponential factor $A = e^{c}\frac{E_a}{R} = 5.478 \times 10^7 \mathrm{m}^{-1} = 9.13 \times 10^5 \mathrm{s}^{-1}$.

The similar procedure has been followed for prepreg and other epoxy resin systems to determine heat of reaction, degree of cure, activation energy and pre-exponential factor. The properties obtained using the DSC test for each material have been given in Table 5. It has been found that as the degree of cure increases, the activation energy of curing slowly decreases. The decrease in the activation energy might have occurred due to the autocatalytic effect in the curing process. The cure reaction depends upon the temperature of cure and characterized by the initial acceleration in the rate of reaction between anhydride and the epoxy, which involves complex kinetics. As the heating rate increases, the autocatalytic reaction becomes faster, reducing the activation energy [37]. The autocatalytic nature can be explained by the transformation of protons. The phenol hydroxyl present in the epoxy resin can afford the acidic environment, therefore, the phenol hydroxyl and the hydroxyl activated by carboxyl could attack the epoxide and methoxy group, which made the cross-linking in intermolecular and intramolecular simultaneously. This transformation of proton assists the reaction between anhydride and the epoxy. Besides, due to the high activity of epoxide, the produced hydroxides are more than the consumed hydroxides. Therefore, these mechanisms could explain that the kinetic model is autocatalytic [38]. The degree of cure and heat of reaction are independent of each other. The activation energy and pre-exponential factor also depend on the degree of cure. The value of the degree of cure for the ARL 136 resin system is only 5% lagging compared to prepreg system. The difference for the degree of cure amongst other epoxy resin systems is almost 40%. The degree of cure for the ARL 136 system is higher compared to other epoxy resin system because of relative reactivity is higher for anhydride compared to phenol, which gives complete curing. The degree of cure strongly depends on the glass transition temperature. The difference for the glass transition temperature amongst other epoxy resin systems is 30–35% as described in Section 3.2. Hence, the difference for the degree of cure turns out to be nearly 40% amongst all epoxy resin systems. The chemical contents of hardener may act as an accelerator in case of ARL 136, which increases the degree of cure.

3.3. Determination of tensile strength

The mechanical testing has been performed using the universal testing machine for all prepared test samples for tensile properties. The composite samples have been cut from the laminates parallel to the *X*-axial direction based on the first layer. The tensile strength of the samples is shown in Fig. 6 and the standard deviations are represented by error bars. For each material, a minimum of ten samples has been tested according to ASTM D638 standard and the mean values of the tensile strength are presented in Fig. 6. The error bar represents the deviation of the tensile strength from the mean value at 95% confidence interval. Thus, the error bars indicate the experimental dispersion of maximum and minimum tensile strength. The change in the tensile modulus of the epoxy is significant above T_g. The tensile strength of the prepreg system is highest compared to all epoxy resin systems. The tensile strength of the ARL 136 resin system is higher amongst other resin systems and almost 6% less compared to prepreg system, whereas the tensile strength difference amongst other resin systems is approximately 16%. The high amount of heat during the curing process for the case of ARL 136 with AH 126 gives complete polymerisation which increases thermo-mechanical properties.

3.4. Statistical analysis

The different epoxy resin systems along with prepreg system have been compared based on optimal thermo-mechanical properties. The simple additive weighting (SAW) method has been employed to perform statistical analysis. The SAW is the most widely used multi-criteria decision making method. The criterion of the method u_i demonstrates the main concept of multi-criteria evaluation methods – the integration of the criteria values and weights into a single magnitude [39]. The performance values ($a_{i,j}$) have been transformed into a scale between 0 and 1 using normalisation procedure (Eq. (5)) for each criteria j, where 1 represents the best performance. The better alternative has been selected by u_i, which is determined by Eq. (6) [40]. In this method, a complete compensation among the criteria is possible.

$$r_{ij} = \frac{a_{ij}}{\max(a_{ij})}, \quad i = 1,\ 2, \ldots, n, \quad j = 1,\ 2, \ldots, m \tag{5}$$

$$u_i = \sum_{j=1}^{m} r_{ij} w_j, \quad i = 1,\ 2, \ldots, n \tag{6}$$

In this study, heat of reaction, activation energy and pre-exponential factor have not been considered as they depend on the degree of cure. The glass transition temperature, the degree of cure and the tensile strength weighting values have been assumed as 0.3, 0.4 and 0.3 respectively as they almost equally contribute in thermo-mechanical properties. The degree of cure represents some other properties also, so the weighting value has been kept a little bit higher. The largest value of the criterion u_i corresponds to the best alternative. The alternatives compared should be ranked in the decreasing order of the calculated values of the criterion u_i. The data obtained have been presented in Table 6. The ARL 136 resin system has an overall 5% deviation compared to the prepreg system.

4. Conclusions

The characterization of epoxy-based composites give high-quality parts with greater consistency and also minimizes the experimental work required to establish a cure cycle for new components. Thermo-mechanical properties of carbon fiber prepreg system along with four different epoxy resin systems have been evaluated. A prepreg system used in the space applications and aircraft industries have been compared with four different epoxy resin systems which can possibly be used for the same applications. The glass transition temperature values have been obtained by DMA analysis, which has been confirmed by DSC analysis. The average difference in glass transition temperatures obtained by both the techniques at the same operating frequency is approximately 5%. The samples made from prepreg are having the highest glass transition temperature among all the selected materials. The samples made from ARL 136 epoxy resin are having a higher T_g among other selected epoxy resin systems as well as almost 3% less compared to the prepreg system. This is because of the mixing ratio of epoxy and hardener as well as specific curing condition. The difference of T_g within epoxy systems is approximately 30–35%. The epoxy resin is exclusively responsible for the experimentally observed exothermic reaction, the heat of reaction and degree of cure for different materials has been estimated using DSC analysis. The activation energy and pre-exponential factors have been acquired using Kissinger's equation. It is found that the activation energy slowly decreases as the degree of cure increases. The value of the degree of cure for the ARL 136 resin system is only 5% lagging compared to the prepreg system. The difference for the degree of cure amongst other epoxy resin systems is almost 40%. The degree of cure for the ARL 136 system is higher compared to other epoxy resin system because of relative reactivity is higher for anhydride compared to phenol, which gives complete curing.

The mechanical strength of each system has been determined using a universal tensile test. The tensile strength of the prepreg system is the highest among all epoxy resin systems. The tensile strength of the ARL 136 resin system is higher amongst other resin systems and almost 6% less compared to the prepreg system, whereas the tensile strength difference amongst other resin systems is approximately 16%. The high amount of heat during the curing process for the case of ARL 136 with AH 126 gives complete polymerisation which increases thermo-mechanical properties. The SAW method has been applied to analyse different epoxy resin systems. The overall thermo-mechanical properties of ARL 136 resin system are within 5% variation of the same properties measured for the prepreg system. This study is very useful for the space applications and aircraft industries and the identified thermo-mechanical properties of ARL 136 resin system would be useful for the composite processing.

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