DIELECTRIC PROPERTY INVESTIGATION OF DEGRADED PRE-PREG AND PERFORMANCE PREDICTION OF THE FINAL COMPOSITE PART

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ABSTRACT

In recent years, fiber-reinforced (i.e., Glass, Carbon, Kevlar) epoxy composites are used widely in structural applications ranging from military and civil aircraft production to recreational consumer products. Most of the industries use pre-impregnated varieties of composite (prepregs) to make high-quality composite parts. Despite their various advantages, prepreg materials are unstable at ambient temperature. A realistic estimation of the shelf life of prepreg is therefore essential for maintaining quality while reducing wastage of resources. Prepregs are temperature and moisture sensitive material systems. To achieve prolonged shelf life, manufacturer and seller of the prepreg must store the materials at zero degrees Celsius (32 degrees Fahrenheit) or in an even colder environment. Once exposed to room temperature or moisture, it starts to degrade and deteriorate in properties.

Broadband Dielectric Spectroscopy (BbDS) is a well-known technique which is widely used for characterization of heterogeneous materials by analyzing the interaction of electromagnetic waves with matter. BbDS can give us the information about change in the molecular structure to the morphological change in the material system.

In this paper, we studied the effects of degradation of prepreg at room temperature for extended periods of time and analyzed their dielectric properties using a BbDS. Later, the relationship between the dielectric properties of the pre-manufactured prepreg and the mechanical strength of the final manufactured composite parts were analyzed to establish a relation.
INTRODUCTION

Prepreg is a common term for fibers pre-impregnated with resin, meaning that the fibers are manufactured and automatically impregnated into a resin matrix, leading to an appropriate ratio between fiber and resin and promoting desired variations in the material properties [1]. A prepreg resin system (epoxy) already includes the proper curing agent, because of which it is ready for lay up without external addition of resin. The cure reactions are initiated once the resin components are mixed and the material is no longer in a stabilized stage, known as stage A, but under transformation, known as stage B. When completely cured, the material attains again a stabilized stage known as stage C [1]. Prepregs have been widely used to produce high quality composite parts. Carbon fiber is lightweight and very strong which makes it a versatile and useful commercial product. Once bound with a polymer or resin, curing the prepreg creates a composite that is then used in various consumer and technical based industries.

Despite their various advantages, prepreg materials are unstable at ambient temperature. Prepreg material is usually kept frozen to prevent degradation. Once exposed to room temperature, it starts to degrade and deteriorate in properties. Unfortunately, the thermal-exposure history of prepreg cannot be strictly controlled. Based on the complexity of the part being laid up, the amount of out-time of a prepreg can be a lot higher during which exposure to moisture affects both how quickly thawed prepreg chemically ages and how it performs during cure. A realistic estimation of the shelf life of prepreg is therefore essential for maintaining quality while reducing waste [2]. To reduce the wastage of the material it is important to determine information about the quality of the prepreg. The prepreg age cannot be accurately correlated by standard quality control tests (e.g., tack, drape). For this an analysis method is needed that is applicable to prepreg material with minimal sample preparation and could be used in the production floor for on-the-spot determinations. Broadband Dielectric Spectroscopy (BbDS) is a robust tool that extracts the material-level information, including the morphology changes caused by micro-detect generation and the orientation of defects in heterogeneous material systems. Raihan et al., Vadlamudi et al., Reifsnider et al., Elenchezhian et al., had successfully used the BbDS to determine the effect of manufacturing defects in a composite and also have predicted the initiation failure in composites [3-8].

Determinations of the effects of prepreg age on finished laminate panels have been investigated a lot in the literature. Scola et al. [9] and Cole et al. [10] found that the short beam strength of laminates decreased with increasing prepreg age. Cole et al. [10] also observed reductions in compressive strength and modulus. The variable success in correlating prepreg age with laminate performance demonstrates that many other factors affect the composite. Cure cycle properties, such as pressure magnitude and its duration, and hold temperature and its duration all affect the resulting composite [11].

To study the effect of degradation of carbon-fiber epoxy prepreg, we kept prepreg samples at room temperature for extended periods of time and manufactured composites out of it to test their mechanical strength and simultaneously examined the dielectric properties using BbDS of the degraded and non-degraded prepreg samples before and after the curing process.
BROADBAND DIELECTRIC SPECTROSCOPY (BbDS)

Broadband dielectric spectroscopy is the interaction of electromagnetic waves with matter, and it has been a popular tool for determining heterogeneous material characteristics. There are a lot of factors that can alter the dielectric spectra of a heterogeneous material, such as the shape and orientation of the combining phases, the morphological homogeneousness as well as the interaction of the electrical and structural properties between the particles. Changes start occurring in the dielectric spectra right from the time it is manufactured to the end of its shelf life, throughout which damage may accumulate inside the materials. This produces data associated with molecular and dipolar fluctuation, charge transport and effects of polarization arising within the boundaries of the material. Maxwell’s equations depict the interaction between electromagnetic fields and matter. A material system is comprised of multiple polarization mechanisms such as ionic (molecular), dipolar (orientational), electronic, interfacial (Maxwell–Wagner–Sillars) polarization and hopping charge polarization [12]. The following Figure 1.1 shows the different types of polarization and their effect on the dielectric response and its corresponding effective frequency range.

![Figure 1: Dielectric response of material constituents at broad band frequency ranges](image)

Polar molecules are contained inside of heterogeneous materials and may have interfaces with different electrical properties. In the presence of an applied electric field it will polarize the material by orienting the dipole moments of polar molecules and charge accumulation at the interfaces of dissimilar materials. The polarization of a linear dielectric is given as:

\[ P = \varepsilon_0 \chi E \]  

(1)
here, $\chi$ = tensor of dielectric susceptibility

$\varepsilon_0$ = dielectric permittivity of vacuum i.e., 8.854*10e-12 F/m

$E$ = Electric Field.

Now, based on Maxwell’s laws of electromagnetism, we have the equation,

$$\nabla \cdot D = \rho$$

(2)

This is also known as Gauss Law, Where, $\nabla \cdot$ = Divergence operator, $D$ = Electric Displacement Field and $\rho$ = Electric charge volume density

The relation between the dielectric displacement and electric field is given as

$$D = \varepsilon_0 E + P$$

(3)

From (1),

$$D = \varepsilon_0 E + \varepsilon_0 \chi E$$

(4)

$$D = \varepsilon_0 \varepsilon_r E$$

(5)

In this case, $\varepsilon_r = (1 + \chi)$ is known as relative permittivity. Finally, we get $D = \varepsilon E$ where $\varepsilon = \varepsilon_0 \varepsilon_r = \varepsilon' - \varepsilon''$ is defined as complex permittivity in which $\varepsilon'$ is the real part of the complex permittivity and $\varepsilon''$ is the imaginary part, in other words the dielectric loss. Thus, we can now plot two graphs, one for the real part of the permittivity and other for the imaginary part, both of which corresponds to the logarithmic values of the frequencies.

**Dielectric Relaxation Strength (DRS)**

Dielectric Relaxation Strength is defined as the algebraic difference between static permittivity value and the limiting frequency permittivity value.

$$\Delta \varepsilon = \varepsilon_s - \varepsilon_\infty$$

The DRS is helpful in determining interfacial polarization. The equation shown above states that, in a heterogenous composite material, the interfacial polarization is higher if the DRS value is higher. Higher DRS indicates more interfacial polarization owing to charge accumulation around boundaries (voids, cracks etc.), indicating a lower mechanical strength which was evident from the previous work [3].

### 2. EXPERIMENTAL PROCEDURE

#### 2.1 Stage I- Dielectric investigation of degraded prepreg

2.1.1 Specimen Preparation

A roll of Toray T700S Plain Weave Fabric Prepreg, composed of carbon-fiber and G-94 epoxy resin, was cut into rectangular pieces of similar dimensions and aged for 10 days. The
samples were kept at room temperature in Ziploc bags, sandwiched between two pieces of parchment-paper to prevent samples from sticking to the bags because of increased tackiness at room temperature. The samples were stored in the lab for further spectroscopic analysis. Before using the parchment paper to sandwich the samples, a sheet of the paper was tested at different points to compare the dielectric properties of the paper and to confirm the consistency in results. The same sheet of paper was cut up into several pieces to be used later with the samples. The samples were then kept in a humidity-controlled laboratory, at room temperature. The samples were named B.

2.1.2 Equipment

An in-house manufactured shielded cage was used to block out electromagnetic waves. The cage was used with a Broadband Dielectric/Impedance Spectrometer, manufactured by Novocontrol, for carrying out the dielectric study. The sample was placed inside the Cage, between two copper electrodes of 1-inch diameter embedded in blocks made of polycarbonate material. This forms the sample capacitor inside the cage. A voltage with fixed frequency is applied to the sample, resulting in a flow of current of same frequency with a phase shift. We analyze the dielectric properties of the sample with the applied voltage and current response. The alpha analyzer measures the permittivity and conductivity as a function of frequency for the applied electric field. Figure 2 shows the equipment setup that was used to carry out the experiments.

![Facility manufactured shielded cage](image)

**Figure 2** Facility manufactured shielded cage

**Stage II- Mechanical Characterization of Cured laminates made of degraded prepreg**

This stage was carried out in five batches.

2.2.1 Specimen Preparation
A roll of Toray T700S Plain Weave Fabric Prepreg, composed of carbon-fiber and G-94 epoxy resin, was cut into 5×7 in rectangles +45 degrees to fiber direction. After curing, all the laminates were cut into coupons as shown in figure 3 and mechanically tested to find out their tensile strength.

Batch 1: Sample C and D (Out-time: 2 days)

- C was kept in Freezer and D was kept at room temperature

![Figure 3. Cured laminates cut into coupons for further tensile testing](image.jpg)

2.2.2 Equipment

A Wabash Compression Heat Molding machine was used to cure the laminates under heat and pressure. The Mechanical Testing Machine (MTS) was used to carry out tensile testing on all the samples. The axial breaking load was noted for the samples and used to calculate their breaking stress. Figure 4, shows a fractured coupon loaded using MTS.
3. RESULTS AND DISCUSSION

Stage 1:

We conducted experiments on several batches of prepregs which have been kept out of the freezer for 10 days and the dielectric response was measured and is plotted below. The trend in the variation of the dielectric response is shown below in figure 5.

![Figure 5. DRS of prepreg samples degraded for 10 days](image)

When we analyzed the data from our stage 1 experiments, we saw that the DRS plot showed a decreasing trend with an increase in the number of days the prepreg was kept at room temperature. The plot shows that with an increase in the number of days, the prepreg started to...
cure itself and over time we observed lower DRS values to substantiate it. The following schematics (figure 6) gives an illustration of the above behavior.

Figure 6. Schematic to illustrate the reduction in the permittivity with increasing crosslinking

In the initial stage, there is no crosslinking in the polymer chains and the ions are free to move in the presence of an external electric field, hence we get a higher dipole moment which in turn shows higher polarization leading to higher relative permittivity (at low frequency). Further, as the prepreg is left outside the freezer, slowly the polymer starts to crosslink and this increases with the amount of time it has been kept at room temperature. When crosslinking starts, the ions are no longer free to move and hence we see a reduction in the relative permittivity with increase in the number of days, as shown in the schematic above.

Stage II:

Both, the degraded and non-degraded samples were cured using compression heat molding, a dielectric study was performed on these samples and were mechanically tested using MTS. Figure 7 shows the trend in the mechanical and dielectric response of the degraded and non-degraded prepreg. The plots have been normalized by dividing the average data by the average non-degraded stress and DRS values, so as to maintain consistency in the results. As a result of the normalization, the non-degraded samples have a value of 1 and every other value will either be equal to, less than or greater than 1.
From figure 7 it is evident that the non-degraded samples have lower DRS when compared to the degraded samples and we see an inverse trend in the breaking stress values. The hypothesis behind this behavior is illustrated below in figure 8.

A degraded prepreg when cured will tend to create manufacturing defects in the process of curing that leads to a lower mechanical strength compared to that of a non-degraded prepreg. Also, due to the presence of these manufacturing defects when an external vector electric field is applied, at low frequencies we will observe charge distribution and accumulation around the defects and
hence higher static (low frequency) permittivity leading to higher DRS compared to coupons made from non-degraded prepregs. Hence, we see a higher DRS in the degraded prepreg coupons correlating to lower mechanical strength and lower DRS in the non-degraded prepreg coupons correlating to higher mechanical strength.

4. CONCLUSIONS

We examined the dielectric response of degraded (kept at room temperature) carbon-fiber epoxy prepregs for 10 days and saw a decreasing trend in the DRS values. This trend shows that with increase in the number of days, the sample undergoes partial crosslinking as a result of which the DRS value decreases. Further, a batch of prepregs were kept at room temperature to measure the effect of degradation on them for 2 days. After 2 days, we manufactured coupons out of the degraded prepregs and also a set of non-degraded (kept in the freezer) and performed the dielectric study. The dielectric tests showed that the value of DRS was higher for the degraded samples as compared to the non-degraded ones. This was a result of defects formed in the degraded samples from being kept outside the freezer. Later, tensile tests were performed on the samples to measure their mechanical strength and observed that the degraded samples were less in strength as compared to the non-degraded samples which validates our hypothesis that defects induce charge distribution in the material system leading to higher DRS corresponding to lower mechanical strength.

Moving forward, we would like to study various other material systems, also we would like to increase the sample size and aging time to quantify a single dielectric parameter to assess the quality of the prepreg, in order to reduce material wastage in the future. Also, we would like to study the effect of ageing of prepreg on the delamination of composite laminates using BbDS.

5. ACKNOWLEDGEMENTS

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6. REFERENCES


