

The Effect of Room-Temperature Aging on Enthalpy and Dielectric Property of Carbon-Fiber/Epoxy Composite Prepreg and the Mechanical Property of Manufactured Composite

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ABSTRACT

Fiber-based reinforced plastics are widely used materials in different industries - e.g., Automotive, Aerospace, Defense- because of their various advantages. The most reliable raw materials for manufacturing fiber-based composites are pre-impregnated reinforcing fiber (prepreg). However, the limitation of using prepreg lies in its instability at room temperature. Prepregs have a specific out-life which sometimes makes the manufacturing process difficult. The objective of this study is to find out a way to investigate the room temperature aging effect on prepreg by analyzing the enthalpy and dielectric properties. In this study, differential scanning calorimetry (DSC) was used to measure the reaction enthalpy in the aged prepreg. The dielectric property of aged prepreg has also been analyzed using broadband dielectric spectroscopy (BbDS). We observed a significant effect on the enthalpy and dielectric properties of the aged prepreg. Furthermore, this study concentrates on how the aging of prepreg can affect the mechanical properties of the final composite parts. This study shows that the manufactured composite from aged prepreg shows inconsistency and a slight reduction in its tensile strength. Finally, a manufacturing strategy is suggested that will minimize the inconsistency of the strength of the final composite part manufactured from aged prepreg.

Keywords: Prepreg, Enthalpy, Dielectric constant, Tensile strength, Shelf Life, Out-Life

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1. INTRODUCTION

Carbon fiber-based reinforced plastics (CFRP) are widely used materials in a wide variety of industries including automotive, aerospace, defense etc. because of their various advantages over traditionally used materials (e.g., metals, alloys, etc.) [1],[2]. Especially, fiber-reinforced composites show a higher strength-to-weight ratio which is one of the most desirable aspects in the aviation and automobile industries [2]. However, the manufacturing of the fiber-reinforced composite is associated with a lot of challenges. In recent times, the most reliable raw materials for manufacturing composite are prepreg; but thermoset prepreg material is unstable at ambient temperature. Mostly, the thermoset epoxy resin systems are affected by the room temperature aging. Prepreg manufacturer recommends storing thermoset prepregs at very low temperatures (-18°C) [3]. However, due to the complex manufacturing process of composite, prepregs are exposed to the room environment even from days to weeks. At room temperature, the prepreg material (the resin part) goes through relatively faster crosslinking process that affects the mechanical properties and the manufacturing process adversely[4]. Also, aging occurs when prepregs are kept in the refrigerator for a long time. The cure advancement in prepreg due to room temperature aging causes a change in the properties of the prepreg that may result in the prepreg to be discarded. Therefore, a simple technique is required that will evaluate the degradation state of prepreg and can be used to predict the tensile strength of the final product. In many industries, prepregs are stored in freezer for a long time, and at one point the prepreg expired their shelf life. In general, shelf life is recommended by the prepreg manufacturer which is the time limit up to which prepreg remains useable[5]. The composite part made from out of shelf life prepreg might not provide proper mechanical strength. The out of shelf life prepreg are usually discarded, costing millions of dollars in loss and cause environmental pollution. However, it is also a matter of our interest to investigate how out of shelf life prepreg affects the mechanical performance.

In past studies, different techniques have been recommended to monitor the aging effect of prepregs. Some researchers worked on infrared spectroscopy and high-performance liquid chromatography to monitor the aging effect and achieved the most success from these techniques [6], [7], [8]. However, these techniques involve complex peak interpretation and time-consuming sample preparation that might not be feasible in industry level practice. Differential scanning calorimetry (DSC) is an acceptable characterization tool for monitoring the prepreg aging[9]. Many thermophysical properties can be measured by DSC which act as an indicator of prepreg aging. In one study, it has been shown that the glass transition temperature of resin linearly changed with aging time [10]. However, Firgioni et al observed no change in the glass transition temperature with the aging time for bismaleimide matrix prepreg [11]. In another study, tangent delta curves were analyzed from DSC data with findings of no major changes for the aged prepregs [12]. In this study, the change in enthalpy is measured from the heat flow curve of DSC and a correlation between aging time and the change in enthalpy has been found. However, this technique requires lengthy experimental procedures and repeated experiments to ensure the proper heat reaction. Alternatively, a more convenient and less time-consuming technique has been explored in this study which involves measurement of the dielectric properties of the aged prepregs. Recently, dielectric analysis was used in monitoring prepreg aging which require ion viscosity measurement by heating the sample to cure temperature (destructive method) [13]. In our study, a dielectric constant measuring technique was used which requires a sinusoidal electric field to be applied across the sample for measuring the complex permittivity of the prepreg at different

frequencies level. These dielectric properties can be used to predict the degradation state of the prepreg. Furthermore, by monitoring prepreg aging, tensile strength of composites manufactured from aged prepreg can be predicted. Previously, many studies were done to understand the effect of prepreg aging on the mechanical properties of the manufactured composite. Ji et al showed that there was no consistent relation between the mechanical properties and prepreg aging. Based on their study, flexural and tensile properties of the laminates manufactured using aged prepreps were poor and unpredictable than ones made from non-aged prepreps [9]. Cole et al did not find any significant effect of aging on tensile properties of composite though reductions in compressive strength had been found [7]. Another study showed the fiber/matrix interface could be adversely affected by the moisture. So, during the storage period in-room environment, moisture absorption might occur, and it would affect the mechanical properties of composite. These phenomena cause the delamination of the composite part during tensile loading[14]. João Pedro et al. couldn't reach any specific conclusions based on their study on the aging effect on shear stress and tensile modulus [15]. Akay also reported no significant effect from prepreg aging in interlaminar shear, flexural, compressive and impact strengths of as-cured composite manufactured from aged prepreg [16].

In this study, DSC was used for monitoring the prepreg at room temperature. The changes in enthalpy from the heat flow curve was measured by integrating the area under the peak of the DSC thermograph. Moreover, Broadband dielectric spectroscopy (BbDS) was used to monitor the prepreg aging which could be a time-efficient and effective technique for industry application. The authors also used Fourier transform infrared spectroscopy (FTIR) to get an insight into the chemical shift during aging. Finally, the tensile strength of the final composite part manufactured from different aged prepreps was measured, and a manufacturing technique was suggested which reduces the aging effect on the final composite part.

2. EXPERIMENTATION

2.1 Sample Preparation

In this study, CYCOM, 5320-1 T650/35 3k, an epoxy based thermoset resin system has been used to investigate the room temperature aging effect on prepreg. The prepreg used in this experiment has already expired the shelf life. However, the prepreg was stored in freezer at -18°C for a long time. So, we were investigating how these prepreps without shelf life react when exposed them at room temperature. In this study, the prepreg stored in refrigerator has been considered as nonaged prepreg. Some prepreg samples were kept in room temperature for aging which has been mentioned as aged prepreg. Firstly, the prepreg samples were cut into square pieces and stored at room temperature for up to 60 days to investigate the aging effect. Each sample was placed in a separate ziplock bag to prevent samples from sticking with each other and to avoid infusion of dust and impurities from the environment. To maintain proper moisture and room temperature (25°C), the ziplock bags were put inside a moisture-controlled desiccator. These samples were analyzed at various intervals to monitor properties in prepreg with aging. DSC, FTIR, and BbDS were used to characterize the prepreps at different intervals to investigate the aging effect. To investigate the aging effect on mechanical properties, composite panels were made using compression molding. For manufacturing the composite panel, four plies of prepreg lamina were stacked in a 0-degree

fiber orientation. A proper curing cycle was followed as suggested by the prepreg manufacturer. The sample was cured at 275°C temperature with 3°C/min heating rate for 188 minutes. After making the composite panel, a water jet cutter was used to cut coupons with 10inch ×1inch dimension. During tensile testing, the gage length and grip length were maintained 6inch and 2 inches respectively for every sample according to the ASTM standard[17].

2.2 Differential Scanning Calorimetry:

Differential Scanning Calorimetry (DSC) is a material characterization tool used to measure the amount of heat flow required to increase the unit temperature of a sample [18]. The heating chamber of DSC comprises of a sample pan and a reference pan [19]. It compares the heat flow rate of the sample with the reference. In this experiment, DSC 25 from TA instrument was used to carry out all the tests. The sample weights were maintained from the range of 5-15 mg. The reference pan was kept empty to simplify the testing procedure. When any reaction or phase change occurred in the sample, the heat flow rate changes. The DSC thermograph represents the difference in the amount of heat flow between sample and reference. DSC is an extremely useful to investigate the curing process and to extract important information regarding the cure mechanisms of polymers.

2.3 Fourier Transform Infrared Spectroscopy:

Fourier Transform Infrared Spectroscopy (Nicolet-6700) has been used to assess the presence of the chemical compounds quantitatively in the prepreg. All the scans were collected in the transmission mode with a resolution of 4cm⁻¹. The data was collected at wavenumber ranging from 4000 cm⁻¹ to 650cm⁻¹. A spectrum is produced by making the average of the absorbance values at each wavenumber scanned by the 32 scans. Moreover, a minimum of three readings was taken at different spots of the sample to ensure accuracy.

2.4 Broadband Dielectric Spectroscopy:

In this study, Novocontrol broadband dielectric impedance spectrometer was used to measure the dielectric properties of prepreg. The dielectric impedance spectrometer is attached to an alpha analyzer that measures the complex dielectric and impedance properties of a material as a function of frequency. During the experiment, the sample was installed between two electrode blocks that formed a simple parallel plate capacitor where the sample acts as a dielectric material between the electrodes. A sinusoidal voltage (1 volt) is applied with varying frequency to the sample, and the alpha analyzer measures the dielectric properties of the sample. In general, a phase shift between current and voltage occurs that can be measured by the phase angle. The phase shift of voltage (U_o) and current (I_o) can be expressed by the following expression.

$$U(t) = U_o \cos(\omega t) \quad (1)$$

$$I(t) = I_o \cos(\omega t + \theta) \quad (2)$$

Here,

$$I_o = \sqrt{(I')^2 + I''^2} \quad (3)$$

$$I^* = I' + iI'' \quad (4)$$

$$\tan(\theta) = \frac{I'}{I''} \quad (5)$$

The impedance of the sample capacitor can be expressed as follows,

$$Z^* = Z' + iZ'' \quad (6)$$

Again,

$$Z^* = \frac{U_o}{I^*} \quad (7)$$

The permittivity can be calculated from the following expression if we know the capacitance of an empty sample capacitor,

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' \quad (8)$$

And,

$$\varepsilon^* = \frac{-i}{\omega \times Z(\omega) \times C_0} \quad (9)$$

Carbon fiber and glass fiber composites are dielectric materials. The material state information can be achieved by observing the dielectric relaxation and polarization mechanisms in an electric field. In heterogeneous systems, the number of dielectric relaxation mechanisms is driven by different interfaces, inclusion shapes, and vector directions of an applied electric field [20].

3. RESULTS

The prepreg aging can be tracked by measuring the degree of curing which simply means the conversion of resin state. An estimate of crosslinking reaction rate can also be obtained from the degree of curing. The enthalpy change and activation energy are important factors in the curing process. This study concentrates on enthalpy change during curing of resin which is defined by the amount of energy released or absorbed during a certain reaction. Using dynamic DSC scan and comparing the thermograph of aged prepreps with nonaged prepreg, the degradation state of the prepreps can be analyzed. Figure (1) shows the dynamic DSC scan for different aged prepreps. Here, the peak at 217°C indicates the occurrence of cure reaction of the resin system during the heating of the sample inside the DSC chamber. For each case, the peak can be characterized as the indicator of maximum curing reaction at the corresponding temperature. Subsequently, the measurement of area under the thermograph represents the change in enthalpy. Table (1) shows the changes in enthalpy measured from the DSC thermographs for different aged samples. It can be discerned that enthalpy change during a cure reaction has an inverse relation with the aging of the samples. This can be attributed to the cure advancement which occurs due to the crosslinking

reaction during aging. During the crosslinking process, polymer chains start connecting with adjacent polymer chains.

Table 1: The change in enthalpy measured from the DSC thermograph for aged preregs.

Prepreg condition	Nonaged Prepreg	Aged 15 days prepreg	Aged 30 days prepreg	Aged 60 days prepreg
Enthalpy Change (J/g)	111.57	98.182	94.65	57.595

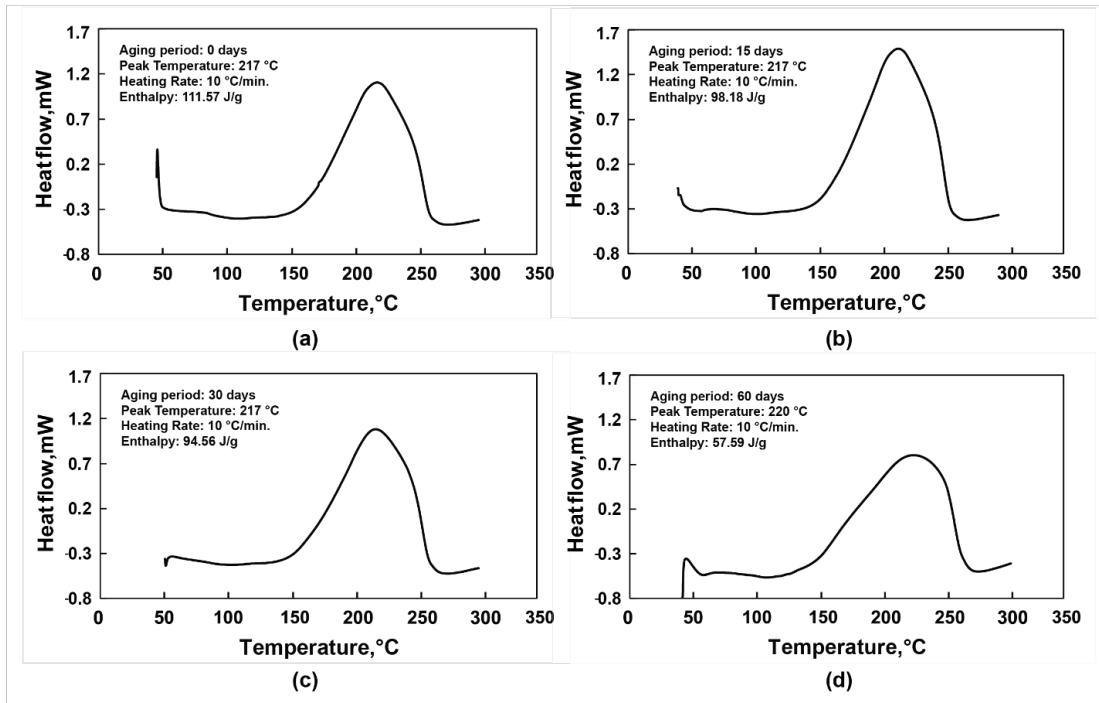


Figure 1: The dynamic DSC thermograph for different aged prepreg. (a) Non-aged prepreg, (b) 15-days aged prepreg, (c) 30-days aged prepreg, (d) 60-days aged prepreg

Therefore, the polymer chain length increases, followed by the break of oxygen due the resin system reaction with the hardener. As the crosslinking advances with time, it causes more conversion of resin, so the concentration of resin decreases with aging. This reduces the rate of cure reaction which in turn results in the reduction of enthalpy change [21]. A similar observation was found from the reverse-phase liquid chromatography study, it was found that the reaction between epoxy-amine increased significantly over the first 30 days, but then the reaction got slower because of higher-molecular-weight products [7].

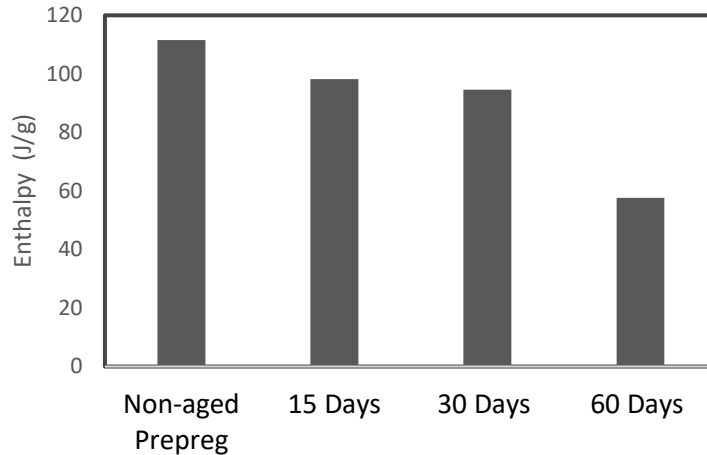


Figure 2: The change in enthalpy with prepreg aging

A similar decreasing trend was observed in the change of enthalpy at 5°C/min heating rate for different aged prepregs. Therefore, the measurement of enthalpy change during curing can conclusively detect prepreg aging.

Consequently, FTIR has been used to understand the chemical shifts that occur during cure advancement for different aged prepreg. To simplify the analysis, the FTIR absorbance curves for non-aged and 60 days aged prepregs have been presented in Figure (2).

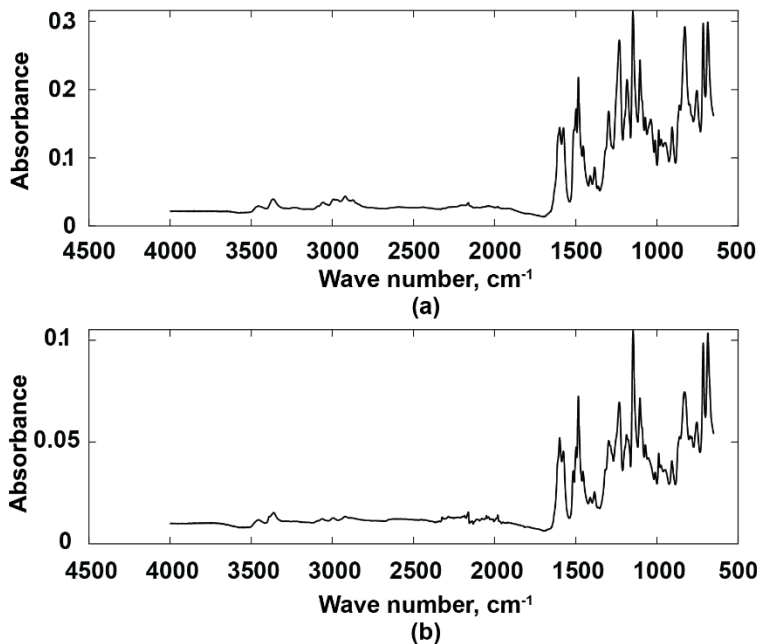
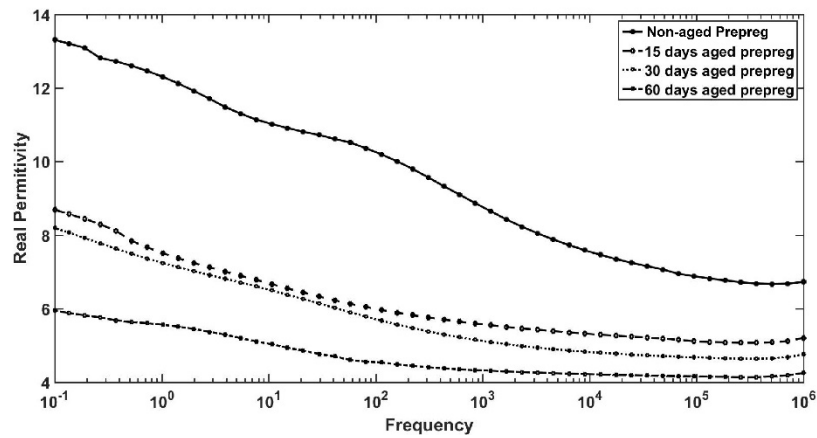


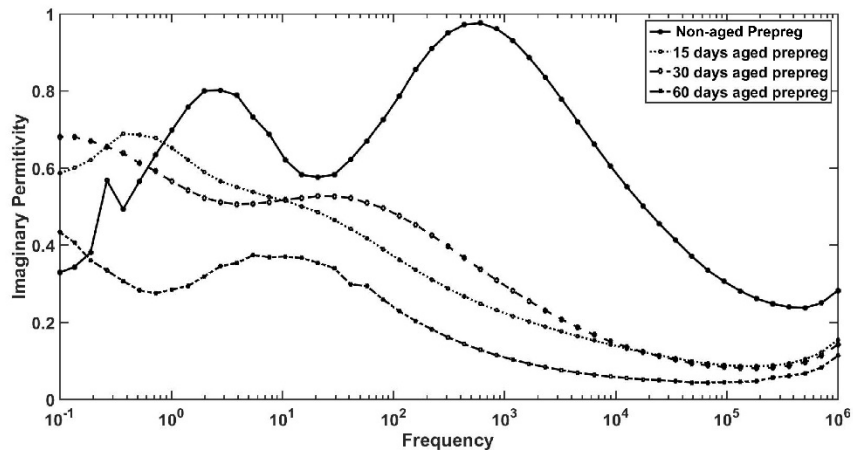
Figure 2: (a) FTIR spectra for nonaged prepreg, (b) FTIR spectra for 60 days aged prepreg

The peaks observed at the range of 1035 to 1100 cm^{-1} wavenumber confirm the presence of the methyl phenyl sulfone which occurred due to the aromatic sulfur oxygen group [22]. The presence of the olefin functional group was observed due to phenyl conjugated carbon-carbon stretching

vibration which generally occurs at the range of 1600cm^{-1} to 1625 cm^{-1} wavenumber [23]. The CH_3 asymmetric stretching vibration and a weak CH_2 absorption peak have been observed at corresponding peaks of 2963 cm^{-1} and 2950cm^{-1} [23]. Absorbance peaks at $1300\text{-}1450\text{cm}^{-1}$ wavenumbers have been observed indicating symmetric CH_3 vibration. A peak at the frequency range of 1550cm^{-1} to 1650cm^{-1} has been observed due to the presence of amine in the hardener[24]. The corresponding peaks observed in the range of $800\text{-}900\text{ cm}^{-1}$ occur due to the presence of the epoxied group [24]. It has also been found that the intensity of the peaks corresponding with the carbon-carbon double bonds decreased with the aging of the prepreg. The dipole moment of -NH_2 and epoxied group also decreased in the aged prepreg. A similar type of finding was observed in past study were using Fourier infrared spectroscopy Cole et al. showed that the number of unreacted epoxy groups decreases steadily at a rate of 0.34% per day [7].



(a)



(b)

Figure 3: (a) Real permittivity and (b) Imaginary permittivity curve for different aged prepreg at various frequency

Though cure advancement of aged prepregs can be monitored using DSC by analyzing the reaction heat or the change of enthalpy, it is not often feasible in the industry due to its lengthy experimental procedure. Furthermore, for accuracy, several samples should be prepared for the test, and the test needs the mass to be only 10-15 mg in weight. But this small amount might not be a proper representation of the entire prepreg system. In this study, we used BbDS to analyze the dielectric property of prepregs which can be used to understand the degradation state of the aged prepregs.

Figure (3) shows the real and imaginary permittivity curves for different aged prepregs at various frequencies. It has been observed that, as the level of curing increases, the dielectric loss peaks (imaginary permittivity) shift towards lower frequencies. Moreover, the real permittivity value of the prepregs also decrease with increased aging. Nandini et al. showed that the dielectric strength of prepregs decreased with the aging effect [25]. These phenomena can be explained based on the relaxation time of polymer chains. The crosslinking enhances the rigidity; however, it also increases the relaxation time. During the BbDS experiment, when AC electric field was applied, the electric field direction alters with a certain frequency. The molecules inside the material also change their dipole direction with the alternating electric field. This phenomenon is called orientational polarization[26]. This type of polarization usually occurs when the frequency range of AC current fluctuates between 1000 to 10^6 Hz [27][25]. In general, the atoms move faster to maintain the dipole direction with changing electric field at higher frequencies. However, the atoms inside the material have inertia that causes a reluctance to move with changing electric field[26]. So, the molecules work against the electric field at higher frequencies causing a loss which is known as dielectric loss. When polymer chain gets large due to the crosslinking process, even at lower frequencies polymer chains show reluctance to orientate with the electric field, increasing the relaxation time. So, the orientational dielectric loss shifts at a lower frequency for aged prepregs. Another explanation can be given by considering the atomic structure of the resin system.

From FTIR data, we found that there was a presence of a ring-like structure in the resin system. We know aromatic rings are considered highly polarizable [28]. Therefore, non-aged prepreg showed a high dielectric constant value because of the presence of pi bond inside the ring structure. The pi bond is responsible for high dielectric constant because of loosely bonded electrons that can move easily[26]. However, during aging, the pi bonds break which reduces the polarizability.

In this study, some composite panels were manufactured from prepreg (out of shelf life) directly taken from the refrigerator. The average tensile strength has been found 921 MPa which is similar to the tensile strength of the composite part manufactured from prepreg with shelf life. According to the manufacturer of CYCOM, 5320-1 T650/35 3k, the tensile strength of the composite part made from fresh(with shelf life) prepreg should be in the range of 810 to 940 MPa [29]. The focus of this study is to observe how room temperature aging affects the tensile strength of the final composite part. Therefore, the out of shelf life prepreg was aged in room temperature for several days, and after that composite parts were manufactured from that aged prepreg. We performed several tensile tests using MTS machine, and from the test results, we found a decreasing trend in tensile strength with the aging effect (Figure 4). More experimental data are required to confirm these conclusions. Besides strength, aging might affect the failure mode of the composite part. We found that the standard deviation for the tensile strength of the composite made from non-aged prepreg was very small. It is always safe to use non-aged prepreg for manufacturing composite

parts because the tensile strength of the final part made from non-aged prepreg is very consistent and can be predicted with very high accuracy. However, the composite panel made from 60 days aged prepreg showed a large standard deviation because of inconsistent breaking load during testing. This is a challenge to predict the tensile strength of the composite made from the aged prepregs with high accuracy.

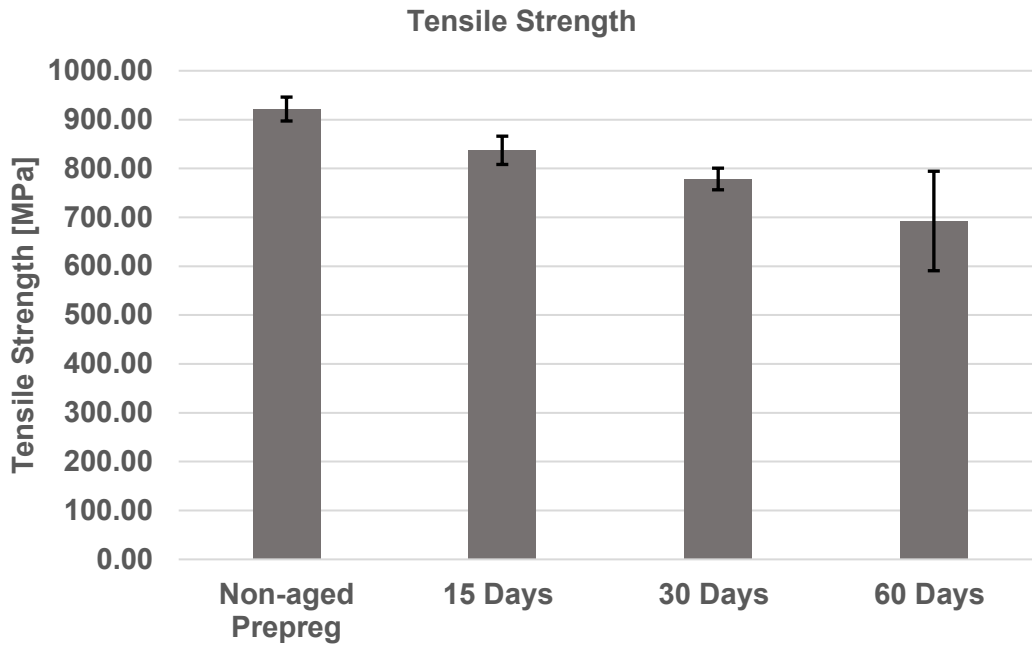


Figure 4: Ultimate tensile strength for composites manufactured from different aged prepregs

During our manufacturing process in the compression molding system, it has been observed that pre-loading on prepreg before starting the curing cycle reduces the inconsistency and increases the tensile strength of the composite part made from aged prepregs. Before the start of curing in compression molding, we applied load on the prepreg lay-up for a certain time at room temperature.

In figure 5, comparison of tensile stress of the composite parts made from 60 days aged prepreg with pre-loading has been compared- without pre-loading and from non-aged prepreg. We found relatively higher strength and consistency in the tensile strength for the composite part made from 60 days aged prepreg with pre-loading compared to sample made without using pre-loading.

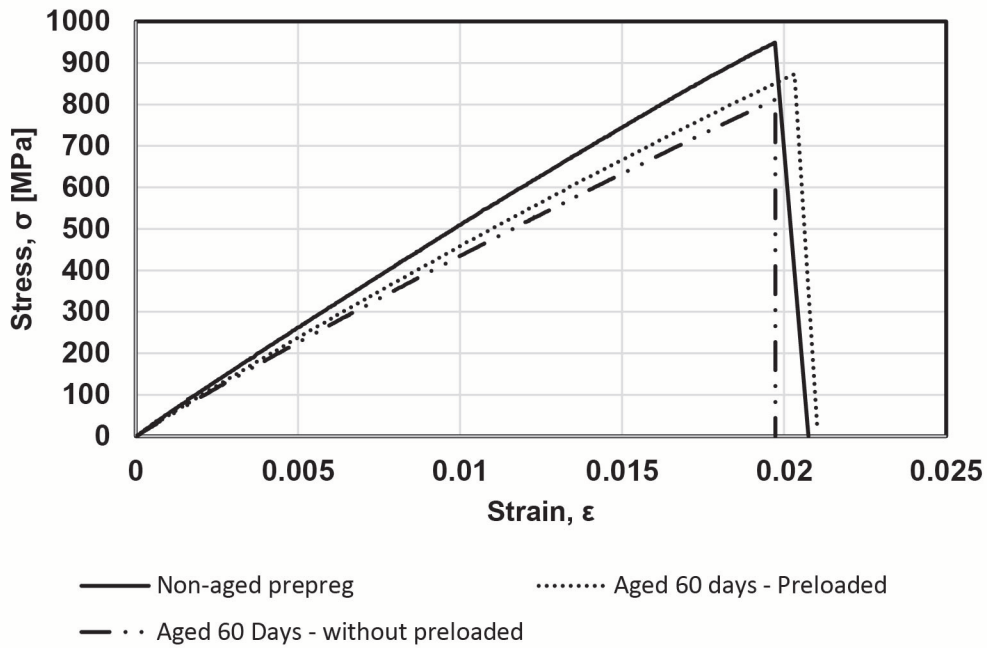


Figure 5: Comparison of the composite made from 60 days aged prepreg with pre-loading, without pre-loading, and with the composite manufactured from non-aged prepreg

4. CONCLUSIONS

Many industries opt for using prepregs for composite manufacturing due to its easier and faster manufacturing process. However, at the end of prepreg shelf life, the materials are usually discarded, costing millions of dollars in loss and have some adverse effect on the environment. Therefore, a convenient tool is necessary that can be used to track the prepreg aging/degradation. Furthermore, based on the degradation state of the prepreg, the mechanical performance of the final composite part can be predicted. In this paper, we showed two techniques for monitoring the prepreg aging- measuring the change in enthalpy and analyzing the dielectric property of the prepreg -both of these techniques can be used to easily track the prepreg aging/degradation. Considering the industry application, using BbDS tool to monitor the prepreg aging is a relatively more feasible and less time-consuming process. It is also important to predict the tensile strength of the final product with high accuracy. However, further studies are required to get a direct quantification of lower mechanical performance. In this research, we showed that composite part manufactured from aged prepreg shows inconsistency in tensile strength. A manufacturing technique similar to debulking was suggested for a compression molding system that will reduce the inconsistency and increase the tensile strength of the final product made from the aged prepreg. The application of this method not only can reduce the wastage of prepreg but also can open new door of possibilities in various secondary applications for out of shelf life prepregs.

5. ACKNOWLEDGMENTS

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Reviewer's Comment

Thank you for taking time to review my manuscript. I revised my manuscript based on your comments. Here, I am also trying to address all your questions.

1. How does this fit into the category of Composites 4.0?

Ans: We just realized that we have submitted in the wrong category. So, we requested to change this to "Sustainability and Recycling Applications" track.

2. What is considered an "aged" prepreg? Is it one that has surpassed the out-time listed by the manufacturer? Likewise, what is considered "fresh" prepreg?

Ans: Most of the time prepreg manufacturer recommend storing prepreg below freezing temperature. Every manufacturer suggests a time limit for room temperature exposure which is known as out life. In general, the out time for Cycom 5320-1 is 20 days at room temperature. However, what will happen when prepreg will expose to room temperature? According to the literature, the resin system in prepreg will start crosslinking and thus aging occurs. We designed our experiment to understand the effect of room temperature effect on prepreg. So here aged prepreg refers the prepreg which has been exposed to room temperature for a different length of time (15,30,60 days). It was my mistake to use the word "fresh prepreg", rather it should be nonaged prepreg which mainly stored in freezer. We directly took out the prepreg from freezer and performed our required test.

3. What thermoset resin systems are most impacted by aging?

Mostly, the thermoset epoxy resin systems are affected by the room temperature aging. However, further study is required to precisely get the answer. Right now, this is not our focus of study; however, we will try to investigate this in our future study.

4. What matrix system is used in the Cycom 5320-1?

Ans: The Cycom 5320-1 is an epoxy resin prepreg system.

5. What is the typical out time for this system?

Ans: According to the manufacturer the out time for Cycom 5320-1 is 20 days at room temperature.

6. How old was the prepreg when you started the study?

Ans: The prepreg we used in this experiment is already out of shelf life. However, the prepreg was stored in freezer at -20°C for a long time. So, we were investigating how this prepreg without shelf life reacts when we expose them at room temperature. In further study, we will be doing the same experiment for prepreg with shelf life. Our main concentration is to investigate how room temperature affects the crosslinking process in prepreg. During investigation, firstly we made composite panel from the out of

shelf life prepreg and found similar tensile strength as we supposed to get if prepreg with shelf life was used to make the composite part. However, when we started aging the prepreg at room temperature, we found lower mechanical performance from the final part.

7. The testing samples you manufactured were not in accordance with ASTM standards. Is there a reason for this?

Ans: For tensile test coupons, we followed 10inch ×1inch dimension. During tensile testing, the gage length and grip length were maintained 6inch and 2 inches respectively for every sample. These dimensions are followed according to the ASTM standard. I am attaching the reference for your considerations.

Reference:

ASTM, Astm D3039/D3039M, Annu. B. ASTM Stand. (2014) 1–13. <https://doi.org/10.1520/D3039>.

8. You are missing equations in section 2.4.

Ans: I corrected all equations.

9. What correlation did you find between all the various testing methods?

Ans: First of all, we used several characterization tools to investigate the aging of prepreg at room temperature. We were exploring the most convenient tools that might be easily used to understand the aging/degradation of prepreg at room temperature. Finally, we investigated how degraded prepreg affect the tensile strength of the final part. Both differential scanning calorimetry (DSC) and Broadband dielectric spectroscopy (BbDs) can be used to understand the degradation state of the prepreg. Using DSC, we measured the enthalpy changes for aged prepreg. Similarly, BbDs was used to measure the real and imaginary permittivity of the aged prepregs. These data revealed the aging effect on prepreg which in terms an indicator of degradation at room temperature. Finally, tensile testing was done to understand how aging of prepreg affects the mechanical performance. Therefore, based on the degradation state of the prepreg, we can predict the mechanical performance of the final composite part.

10. Is your new method able to be directly correlated to a quantification of lower mechanical performance?

Ans: Using broadband dielectric spectroscopy (BbDs), we can easily get a qualitative idea about degradation state of prepreg that might help to decide whether the prepregs should be used in further manufacturing application (may be some secondary application that does not involve mechanical loading). However, we are still exploring this technique and further study is required to get a direct quantification of lower mechanical performance.