

Solvent Analysis of Phenolic Resin Glass Fiber Reinforced Prepreg During Out-time

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The Faculty of the Materials Engineering Department,
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by
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Abstract

Phenolic resin glass fiber reinforced prepregs are highly suitable for airplane interior components due to their high fire resistance, high temperature performance, and low-density characteristics. Safran Cabin seeks to improve their storage of the phenolic resin prepreg during their manufacturing process. The issues the company faces are the occasional delamination of prepreg laminas or the loss of tackiness rendering the lamina unfit for use. The area of investigation was determining the weight loss of volatiles during out-time. The term “out-time” consists of the time the prepreg experiences in transit, on the shop floor, and in short-term temperature-controlled storage. Simulated storage conditions were investigated to three different temperature ranges that the prepreg samples experience during out-time: 2.6°C, 16-18°C, and 28-33°C. The project objective was to better understand the loss of volatiles the prepreg experiences. The volatiles under investigation are from the solvent used in the preparation and manufacturing of the prepreg. The functional groups of key volatiles in the prepreg were detected and monitored using a Fourier Transform Infrared Spectroscopy (FTIR) after different simulated storage periods within the maximum out-time of 11 days. Additionally, Thermogravimetric Analysis (TGA) was used to measure the weight loss of remaining volatiles in the phenolic resin prepregs. The end results of this project suggest that the volatile loss during out-time is more temperature dependent than time dependent.

Key Words: phenolic resin glass fiber reinforced prepreg, prepreg, simulated storage, volatiles, loss of volatiles, composite materials, materials engineering

Introduction

Problem Statement

Phenolic resin glass fiber reinforced prepregs are highly suitable for airplane components due to their high fire resistance, high temperature performance, and low-density characteristics. This is capitalized upon by Safran Cabin who seeks to improve their prepreg manufacturing process. The issue the company faces is the occasional composite delaminates or loss of tackiness rendering it unfit for use. The objective of the senior project was to better understand the volatile loss the prepreg experiences during out-time through solvent analysis to achieve a more consistent product performance.

Background

From automobiles and aerospace applications to buildings and bridges, composite materials are widely used in the modern world due to their high strength, light weight, and other advantageous properties. Engineering composites are manufactured materials consisting of fibers embedded in a matrix. The combination of the fibers and matrix used in a composite has superior, distinctive properties compared to the individual components. [1] The role of the high strength and modulus fibers is to carry loads. The use of matrix between fibers was to separate the fibers as well as transferring loads between fibers. Depending on the type and the orientation of fibers in the matrix, the mechanical properties of composites vary. For instance, a composite with a ceramic type of fibers can provide a different set of beneficial properties from what a polymer-based fiber reinforced composite can produce. Similarly, a composite with longitudinal direction fibers along the loaded force will have an improved performance in mechanical testing compared to a composite with transverse directions fibers.

In this project, the focus composite is a prepreg consisting of woven glass fibers and phenolic resin. To date, glass fiber is the most used reinforcement in polymer-based composites because of their low production cost, excellent mechanical and chemical properties. [1] Two broad categories of polymer matrix in composites are thermoplastic and thermoset. Thermoplastics are polymers with weak secondary bonds connecting between polymer chains. What makes thermoset different from thermoplastic is the three-dimensional network formed by the cross-linking between polymer chains within the polymer structure of thermoset. The structural differences of these polymers determine whether they can be recast or recycled or not. Prepregs are thin sheets of fibers that have been preimpregnated by a thin layer of resin matrix. [1] Phenolic resins, or phenolics, are thermoset resins that are the result of a reaction between a phenol, or substituted phenol, and an aldehyde (Figure 1).

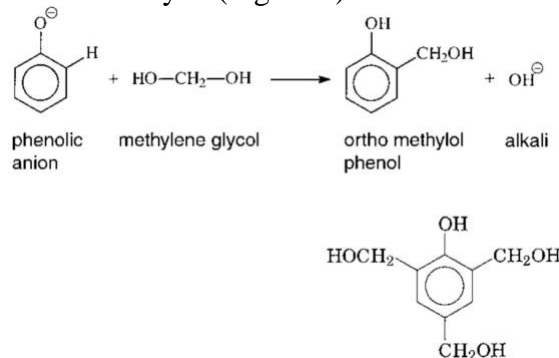


Figure 1. Schematic chemical reaction between phenolic anion and methylene glycol. [2]

There are two categories of phenolic resins, novolacs and resoles. [3] Novolacs are acid-catalyzed, are not reactive, and need a cross-linking agent to complete polymerization. [3] Resoles, the specific type of phenolic resin under investigation, is base-catalyzed and self-curing. [3] Resoles can self-cure due to the presence of reactive side groups on the polymer chains. [3] The key features of manufacturing process parameters of phenolic prepregs are flow, resin content, tack, and volatiles. [2] Some typical volatile solvents in the industry involve methanol, ethanol, isopropanol, and ketones. These volatile solvents evaporate during the curing process as temperature raises. Methylene bridging occurs with resole phenolic resins curing at elevated temperatures (Figure 2). [4]

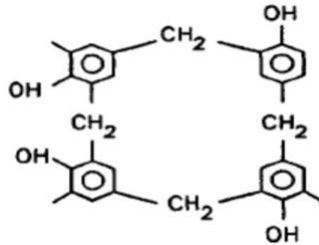


Figure 2. An example of a cross-linked phenolic resole structure which is produced as the curing reaction progresses and methylene bridging occurs. [4]

The loss of volatiles in the late stage of curing can lead to decreases in resin flow and resin tack. More importantly, the loss of volatiles may cause delamination of prepreg layers. There are different types of materials characteristic techniques can be used for the purpose of volatile analysis. In one way, Fourier Transform Infrared (FTIR) Spectroscopy can provide a qualitative measure of the presence of volatiles from the solvent used in the prepreg by monitoring the percent transmittance of key functional groups, hydroxyl and etheric bond (Figures 3).

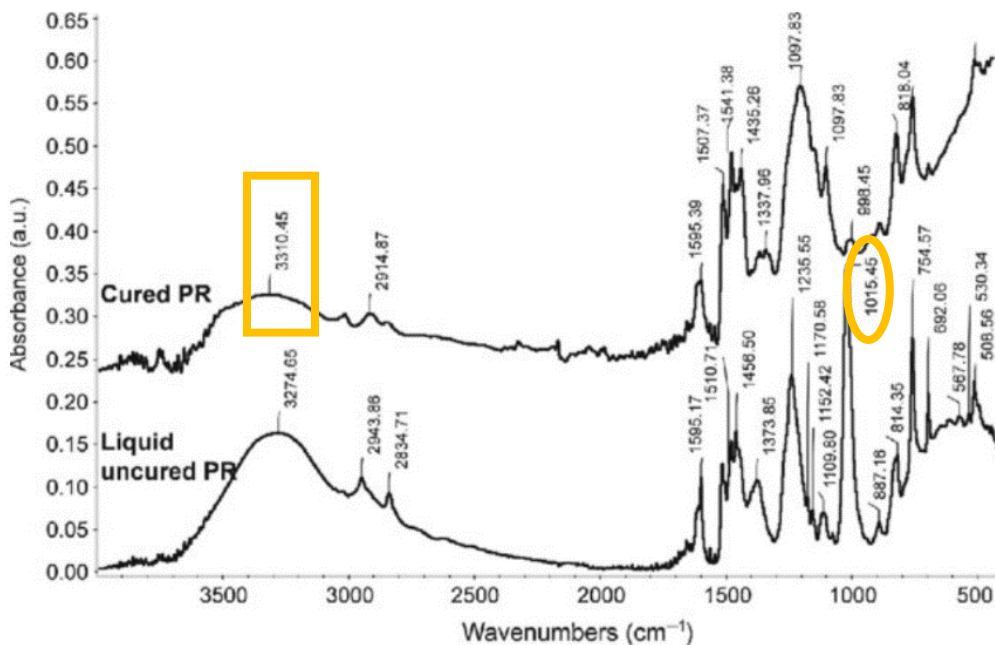


Figure 3. This is an FTIR spectrum that examines absorbance versus wavenumbers, rather than % transmittance. Going from uncured phenolic resin (bottom spectrum) to cured phenolic resin (top spectrum) that absorbance of the notable peak, alcohols and ether bridges, decrease as curing progresses. [5] The peaks at 3310.45, indicated by a square, and 1015.45, indicated by an oval are representative of an alcohol and ether bridge, respectively. [6]

In another way, Thermogravimetric Analyzer (TGA) can measure the loss of remaining volatiles of prepreg under a controlled heat treatment, which provides a quantitative analysis on the presence of volatiles (Figure 4).

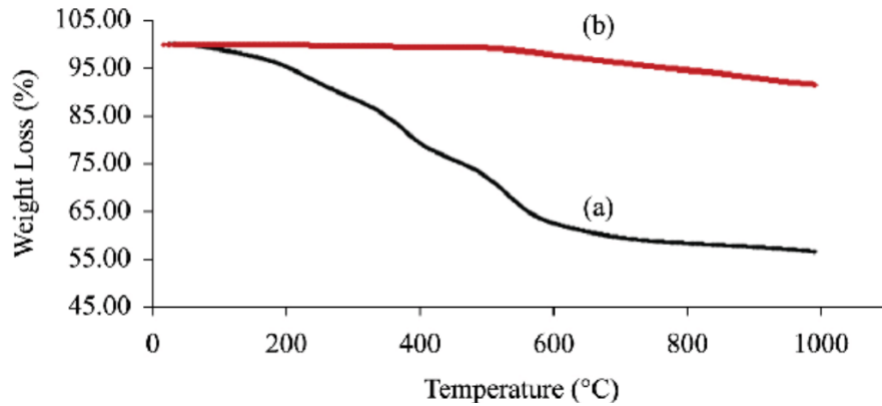


Figure 4. TGA curves of phenolic resin materials showing variation is percent weight loss upon heating: a pure phenolic resin (a) and a cured carbon fiber phenolic resin composite (b). [7]

Manufacturing Process – Prepreg Production & Application Manufacturing

The glass fiber reinforced prepreg under examination has a specific manufacturing process. The first step is the phenolic resin bath where the glass fibers are solution-dipped. [8] In the impregnation bath, the resin is dissolved by the added solvents to reduce the viscosity of the resin for a better manufacture handling of the prepreg. The solution dip technique also benefits the wetting characteristic of the liquid resin, leading to thorough surface contact between the matrix and the glass fibers. The equipment used for the solution dip method is a horizontal solution machine. The prepreg is then delivered into a heat controlling chamber to cure until B-stage (Figure 5).[4] In the impregnation bath, the resin is dissolved by the added solvents to reduce the viscosity of the resin for a better manufacture handling of the prepreg. The solution dip technique also benefits the wetting characteristic of the liquid resin, leading to thorough surface contact between the matrix and the glass fibers. The equipment used for the solution dip method is a horizontal solution machine. The prepreg is then delivered into a heat controlling chamber to cure until B-stage (Figure 5).[8]

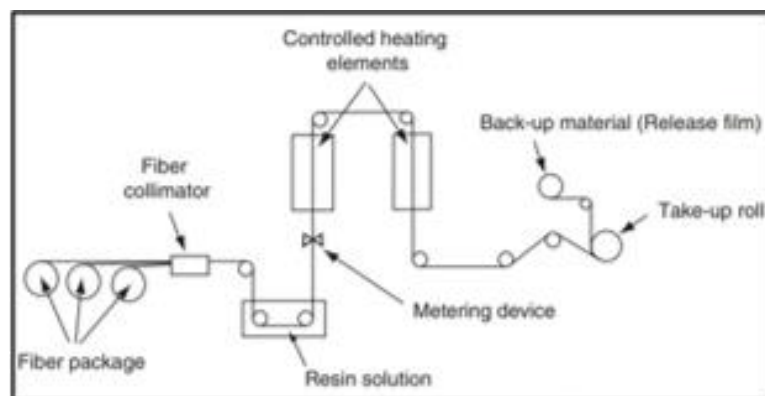


Figure 5. A general schematic of the manufacturing process of prepreg sheets that are cured till B-stage [9].

At this point, the B-staged prepreg is rolled up and prepared for transportation to the customer or company. For Safran Cabin, the received prepreg is shipped in large rolls in non-temperature-controlled trucks. Once they receive it, the prepreg is put into storage at 40°F. The prepreg can remain in this storage for around four months or longer, if kept colder. Once the prepreg is ready for application manufacturing, the prepreg is removed from storage and allowed to warm to room temperature. The prepreg is then laid up in a tool or mold for the specific application design method. For Safran Cabin, their main component that they use this prepreg for is aircraft overhead storage bins.[10] The two methods they use to construct the overhead bins are a matched metal compression molding and vacuum composite layup. From the time the prepreg is removed from storage till cut and manufactured takes up to 3 days.

Out-time is the phrase the company uses to describe the time outside of storage that the prepreg experiences curing from B-stage. Out-time includes transportation time from the prepreg manufacturing site till put in storage at Safran Cabin, the time after storage when it can be cut, and time when it is manufactured for application. The prepreg sheets continue to age as the resin self-cures at room temperature during out time. The tentative limit the company puts on out-time is 10 days before the prepreg is deemed unusable.

Applications

The aircraft overhead storage bins are the most common application for the phenolic resin glass fiber reinforced prepreg at Safran Cabin. An example of an aircraft that they have recently been used in include the A220 (Figure 6).



Figure 6. The phenolic resin glass fiber reinforced prepreg is used in the manufacturing of the overhead cabins of an A220 aircraft. [11]

Prepreg key characteristics include having high temperature performance, long-term durability, and chemical resistant, high fire resistance along with low smoke generation and low smoke toxicity properties. [2] Such superior properties make phenolic resin a promising material for applications including, but not limited to, construction, aerospace, and maritime application. [2]

Experimental Procedure

Simulated Storages

The problem Safran was experiencing is the loss of tackiness in the phenolic resin glass fiber reinforced prepreg prior to compression molding. The loss of tackiness causes the prepreg to improperly laminate during the compression molding process. The improper lamination would occasionally result in delamination. The loss of tackiness arises from a loss of volatiles present in the prepreg from its solvent prior to the manufacturing step. The two factors being investigated that could affect the presence of volatiles were the number of days spent in storage and the temperature ranges. The goal for this project was to perform material characterization on the prepreg as it endures a simulated version of the out-time at the company to determine the extent the two factors have on the loss of volatiles of the prepreg. Three different temperature ranges were used for out-time simulation: 2.6°C, 16-18°C, and 28-33°C. The 2.6°C replicates the company storage at 4.4°C (40°F). (Table I)

Table I. Simulated Storage Temperature Ranges

Storage Temperature	Simulated Storage Temperature Ranges
Short Term Storage at Safran (40°F)	2.6°C
Lower Ambient Temperature	16-18°C
Higher Ambient Temperature	28-33°C

The lower ambient temperature, such as a cool day in winter, experienced on the shipment truck and shop floor was simulated by 16-18°C. A semi-insulated environment was used to prevent major temperature changes. Elevated ambient temperature was simulated at 28-33°C which replicated the temperature prepreg experiences during transport and shop floor on hot summer days. The length of the simulated storages was extended to 11 days, which was beyond the maximum out-time that prepreg experiences at the company. The lengthened simulated storages provided insight to how the temperature and length of out-time effects the presence of volatiles. (Figure 8)

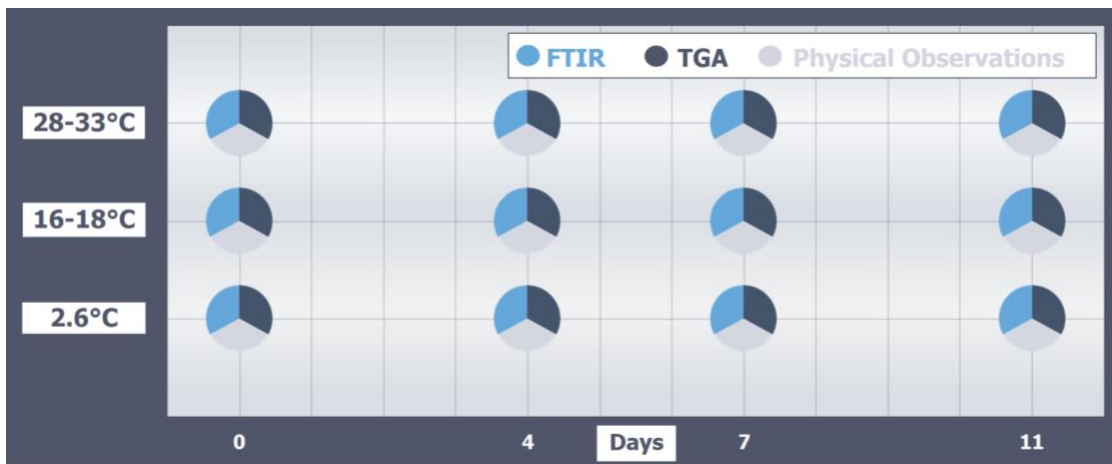


Figure 7. Depiction of the experimental methods of performing FTIR, TGA, and physical observations on day 0 (first day of storage), day 4 of storage, day 7 of storage, and day 11 of storage at the three different temperature ranges.

Sample Preparation

The prepreg would be received in a 3 ft by 5 ft square by an overnight shipment from Safran Cabin in Santa Maria. The roll was then cut into multiple pieces that were about 3 in by 3 in squares. The samples were stored in an equal number of unsealed and sealed polyethylene-based bags. This allowed for a sample to be taken out of a simulated storage at a specific temperature and length of out-time and transferred to a long-term composite storage freezer. The assumption was made that there was no further effect on the samples they were placed in the long-term composite storage freezer. This is due to the low temperature, below 0°C, of the storage freezer.

Testing Methods

The testing methods used to monitor the loss of volatiles included: physical observations, FTIR, and TGA [12-14]. Physical observations were made on prepreg samples upon arrival and between storage length. FTIR and TGA testing was conducted on prepregs as received and throughout storages at different temperatures and length of time. Each testing method was conducted to samples from simulated storages every 3-4 days to replicate the out-time length of 10 days that is experienced by prepreg at Safran. During physical observations, the level of flexibility and tackiness of the prepregs were compared at different storage conditions, namely, sealing condition, storage length, and storage temperature. The tackiness and rigidity of the prepreg samples were scored on a scale of 1-5, with 1 being the original rigidity and tackiness conditions of the prepreg upon delivery and a 5 being a fully cured condition. TGA thermograms of prepregs were obtained from a heating rate of 5°C/min at with temperature range 25-160°C. These testing parameters were similar to the compression molding process used at Safran Cabin.

Lab Safety Precautions

The safety factors of the project included: COVID safety, regular lab safety, and material handling. The safety precautions taken for COVID-19 included scheduling lab time with equipment, wearing proper facial coverings, maintaining proper social distancing, plastic wrap on computer keyboards, and regular disinfecting and cleaning of surfaces. Regular lab safety consisted of long pants, closed-toed shoes, safety glasses, and maintaining a lab safety partner. The prepreg samples were always handled with disposable latex or nitrile gloves. The prepreg was stored in the fume hood during the 16-18°C and 28-33°C simulated storages where out-gassing could occur.

Results

Physical Observation Results

Small decreases in flexibility and tackiness results were observed on prepregs stored at low temperatures (2.6°C and 16-18°C). The samples were ranked on their tackiness (Table II) and rigidity (Table III) rigidity and tackiness whenever they were transferred from simulated storage to the long-term storage composite freezer. However, significant loss of tackiness and rigidity of prepregs were evident after the simulated storage at 28-33°C for 4 days. Starting from

day-7, prepreg stored at 28-33°C lost most of the tackiness and became rigid. To measure the rigidity the samples were manipulated by hand to determine whether the samples were still malleable. The 28-33°C samples were no longer malleable by day-7 and day-11 without cracking. There were no significant differences between the physical rankings of the 2.6°C and 16-18°C samples.

Table II. Physical Observations of Tackiness in Prepreg Samples During Simulated Storages

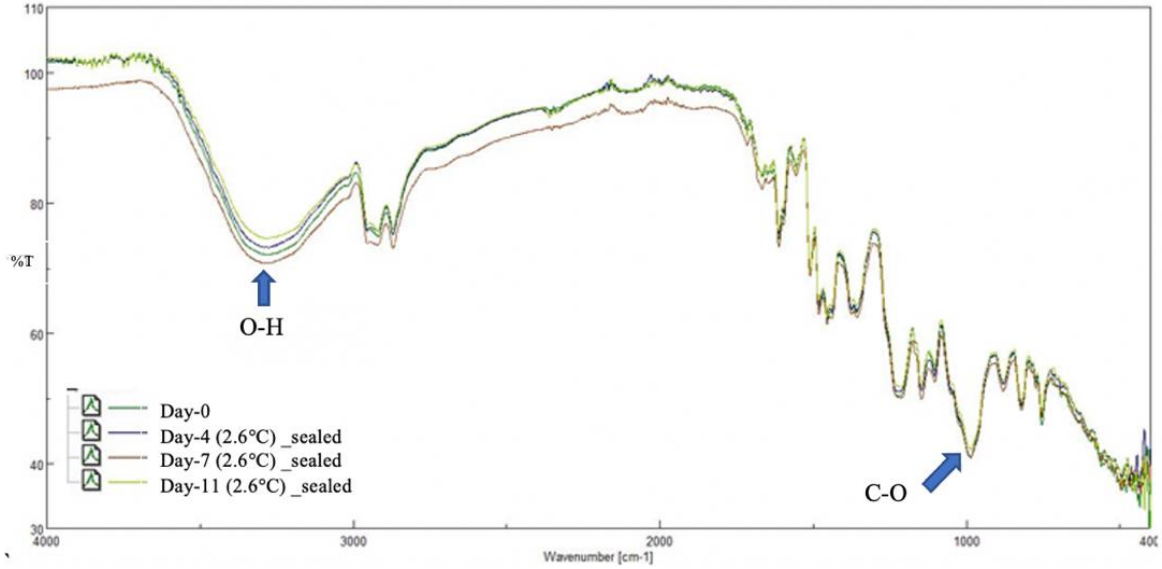
Number of Days in Storage	Refrigerated Temperature (2.6°C)		Room Temperature (16-18°C)		Elevated Temperature (28-33°C)	
	Sealed	Unsealed	Sealed	Unsealed	Sealed	Unsealed
4	1.5	1.5	1.0	2.0	4.5	4.5
7	1.5	2.5	1.5	1.5	5.0	4.5
11	2.5	3.0	2.0	1.5	5.0	5.0

Table III. Physical Observations of Rigidity in Prepreg Samples During Simulated Storages

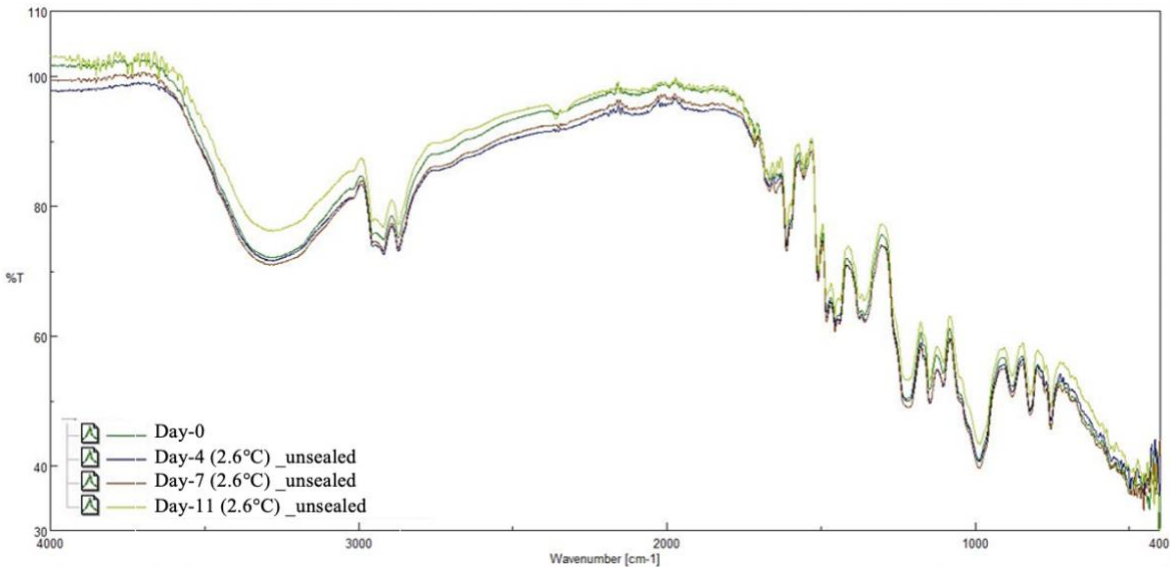
Number of Days in Storage	Refrigerated Temperature (2.6°C)		Room Temperature (16-18°C)		Elevated Temperature (28-33°C)	
	Sealed	Unsealed	Sealed	Unsealed	Sealed	Unsealed
4	1.0	1.0	1.5	1.5	4.0	4.5
7	1.0	1.0	1.5	1.5	5	4.5
11	1.0	2.5	2	2	5	5

FTIR Results

Overlaid FTIR spectra of preregs were compared to determine bond population of the key volatiles in percent transmittance after simulated storages at different temperature ranges and storage lengths. Addition to that, FTIR spectra of prepreg samples in both sealed and unsealed conditions were obtained on samples stored at 2.6°C (Figure 8). The change of percent transmittance of FTIR curves were monitored and compared to the spectrum of day-0 sample on the first day the batch of samples were stored.



(a)



(b)

Figure 8. FTIR spectra of prepreg sample after 11 days at 2.6°C in both sealed (8a) and unsealed (8b) conditions.

Furthermore, overlaid FTIR spectra of prepreps were compared on different days of storage at 16-18°C. The storage conditions sealed versus unsealed was also compared. As a result, a discernible difference on FTIR results between the sealed and unsealed conditions was absent at 16-18°C as compared to day-0 (Figure 9).

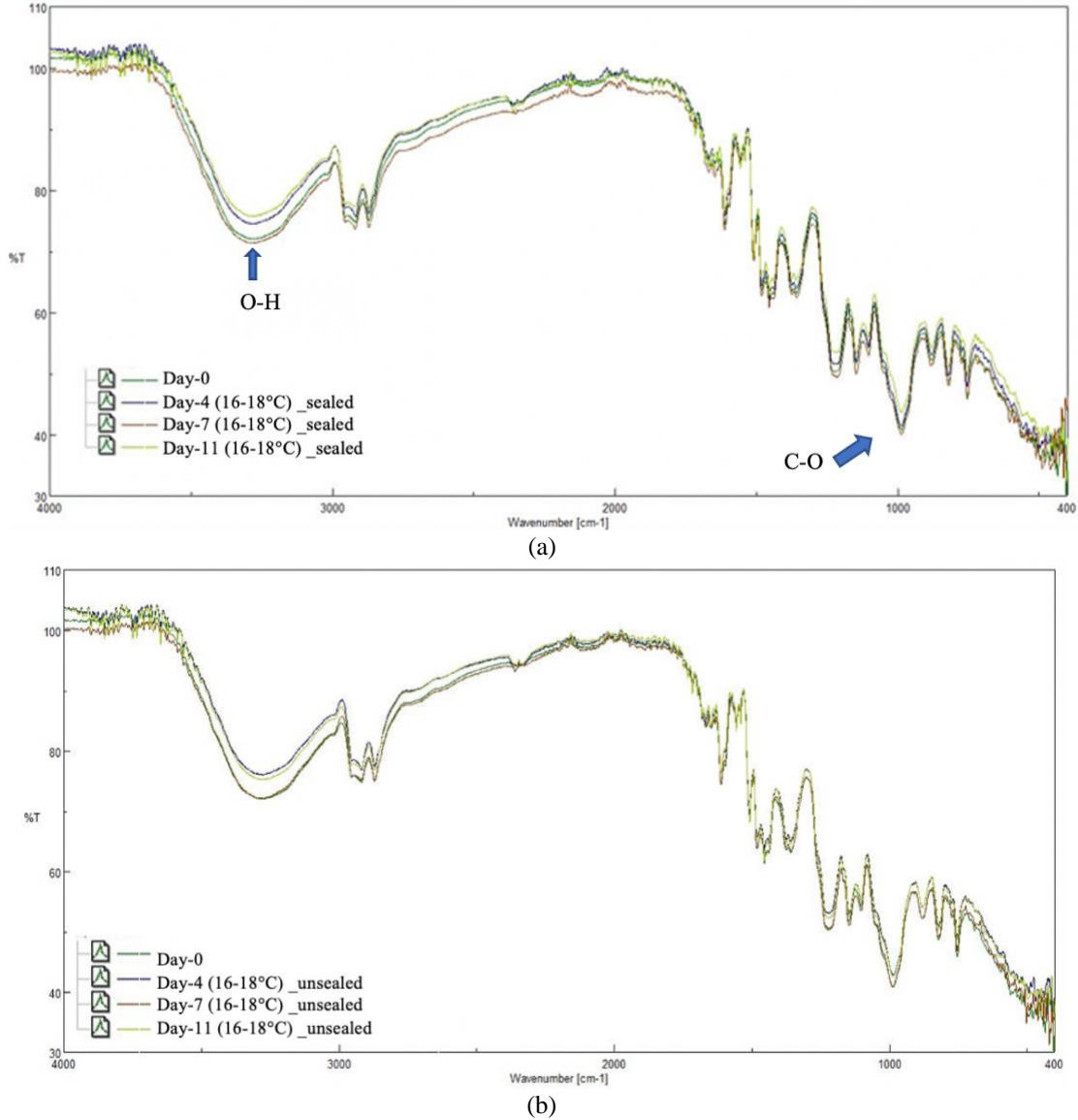


Figure 9. FTIR spectra of prepreg sample after 11 days at temperatures between 16-18°C in the sealed condition (a) versus the unsealed condition (b).

However, the percent transmittance on the FTIR spectra of prepreps stored at 28-33°C increased throughout simulated storages (Figure 10). For the sealed condition, the percent transmittance of the detected functional groups increased significantly after 4 days of storage, implying the elevated temperatures had a great influence on the presence of volatiles (Figure 10a). The percent transmittance of volatiles continued to increase observed on FTIR spectra on day-7 and day-11. For the unsealed condition at 28-33°C, the percent transmittance of volatiles detected on day-4, day-7, and day-11 prepreg samples were close to 100%, meaning that the volatiles loss in prepreps under the unsealed condition was remarkable (Figure 10b).

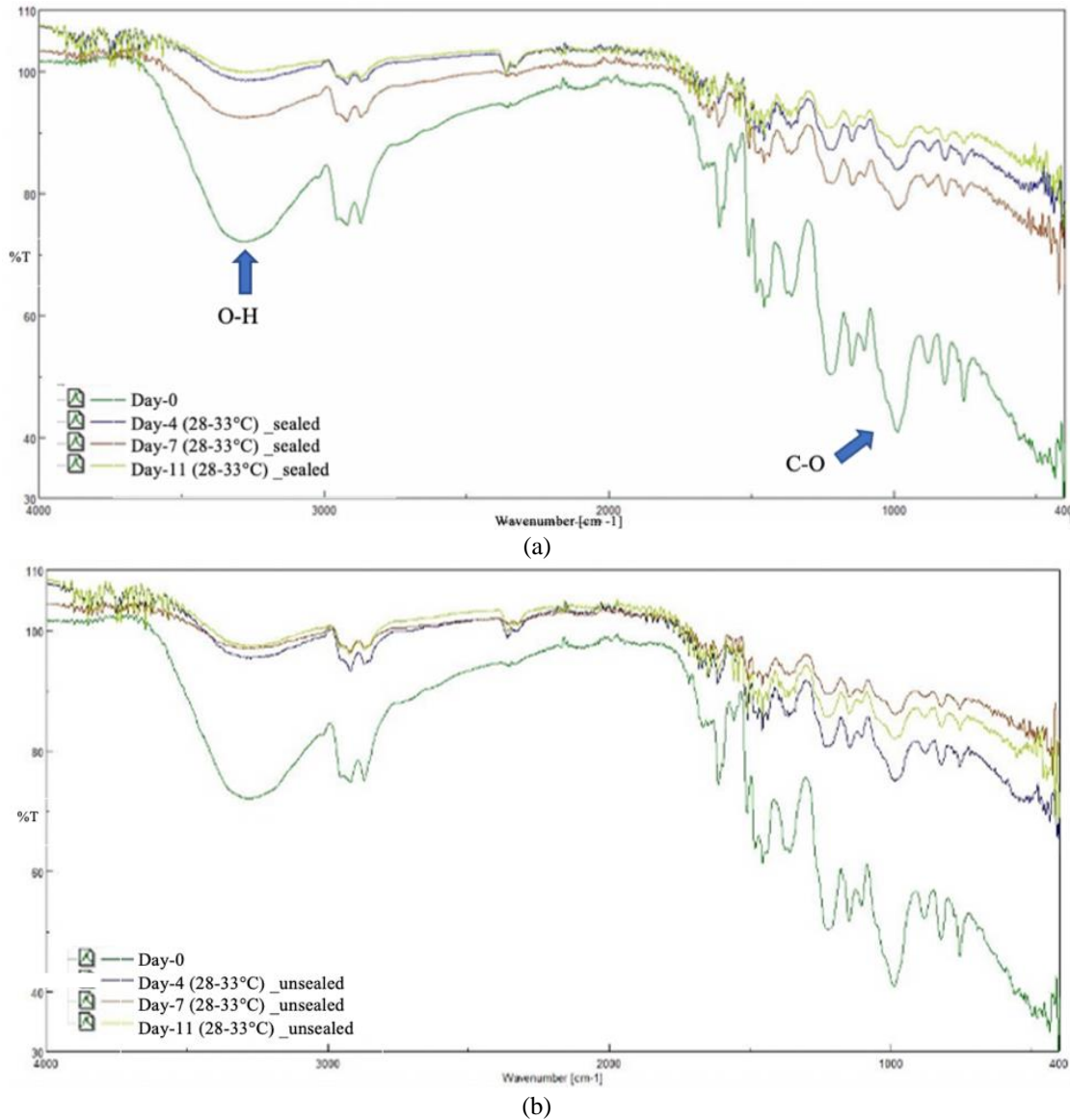
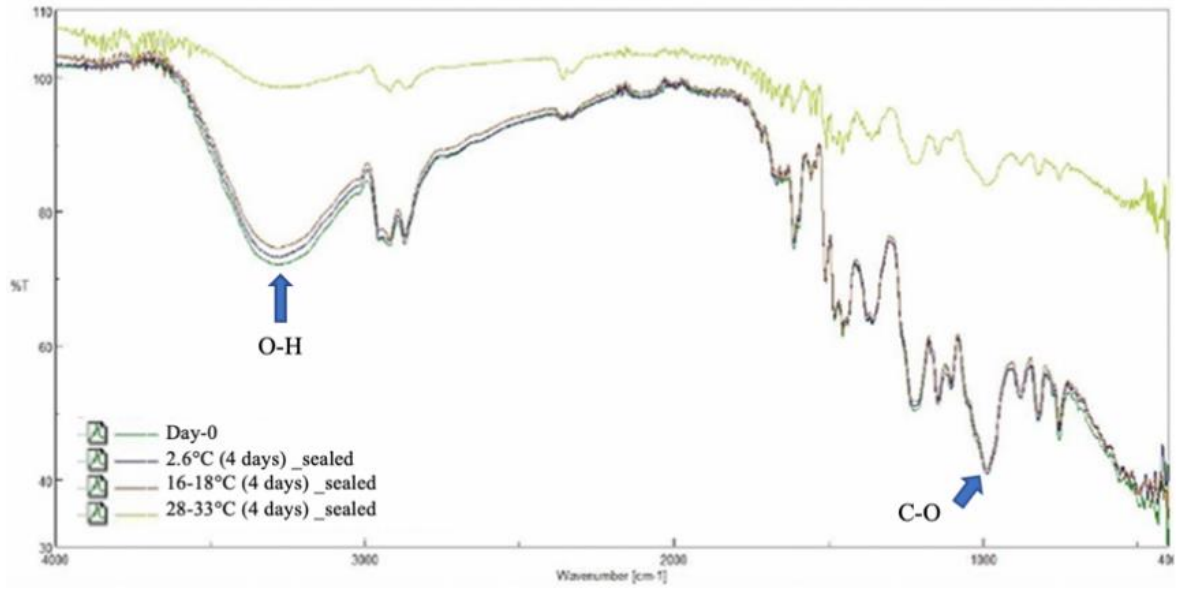
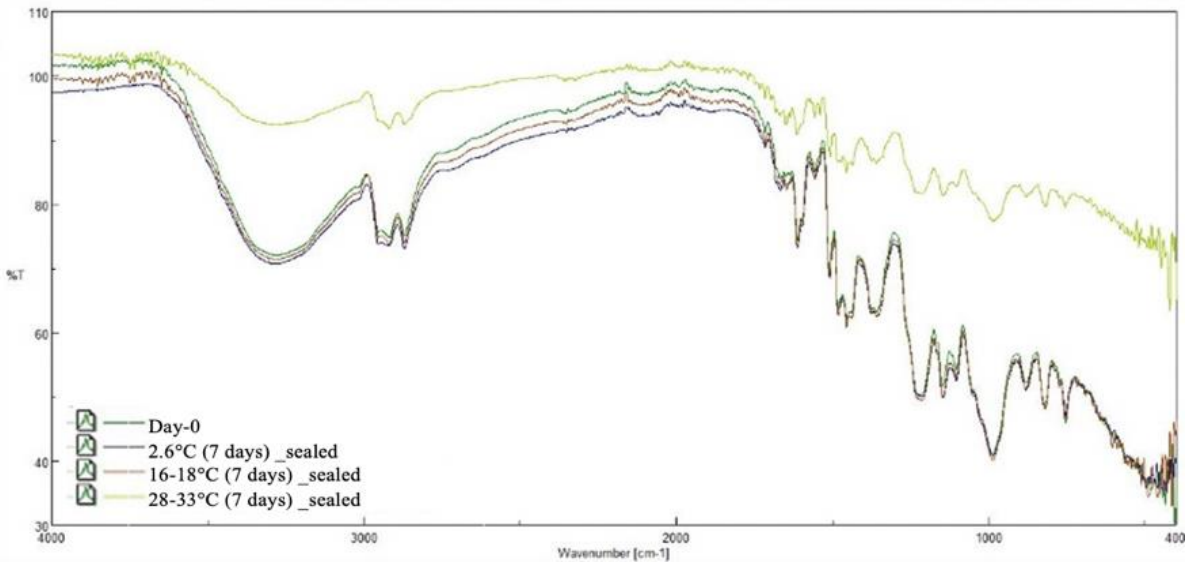


Figure 10. FTIR spectra of prepreg samples showing significant changes in percent transmittance of volatiles after 11 days of simulated storage at 28-33°C in both sealed (a) and unsealed (b) conditions.

Additionally, FTIR spectra of prepregs were overlaid to compare the change in peak intensity at the same storage period but different storage temperatures (Figure 11). The highest percent transmittance of volatiles was observed on the FTIR spectrum of the prepreg sample stored at 28-33°C in the sealed condition. This trend was spotted on the overlaid FTIR spectra of prepregs throughout 11 days of simulated storages.



(a)



(b)

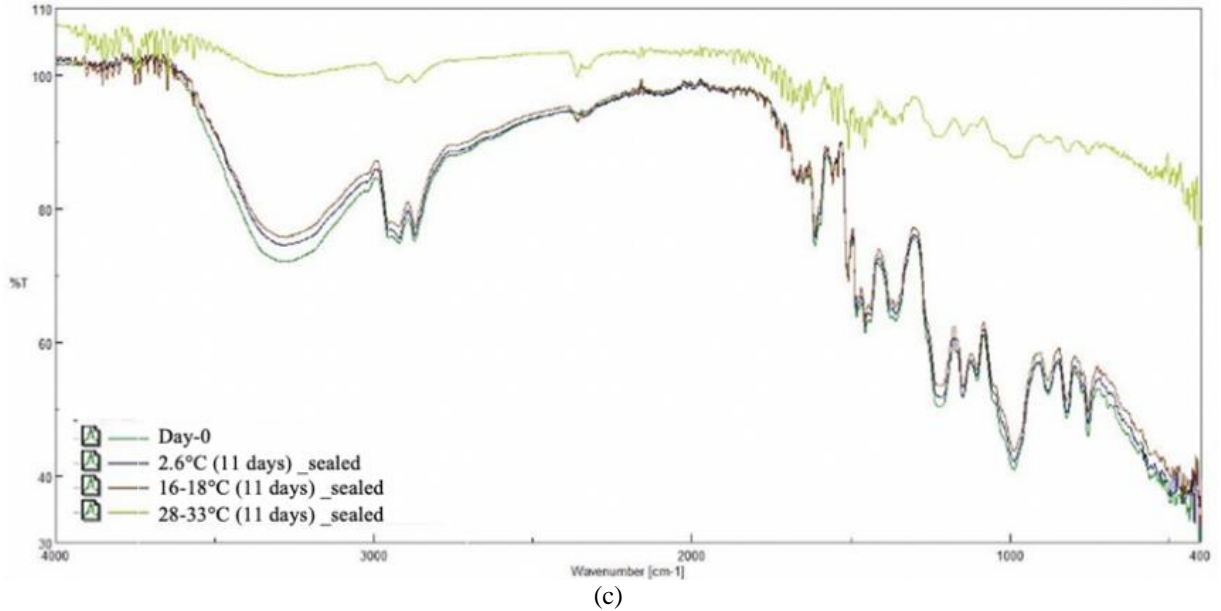
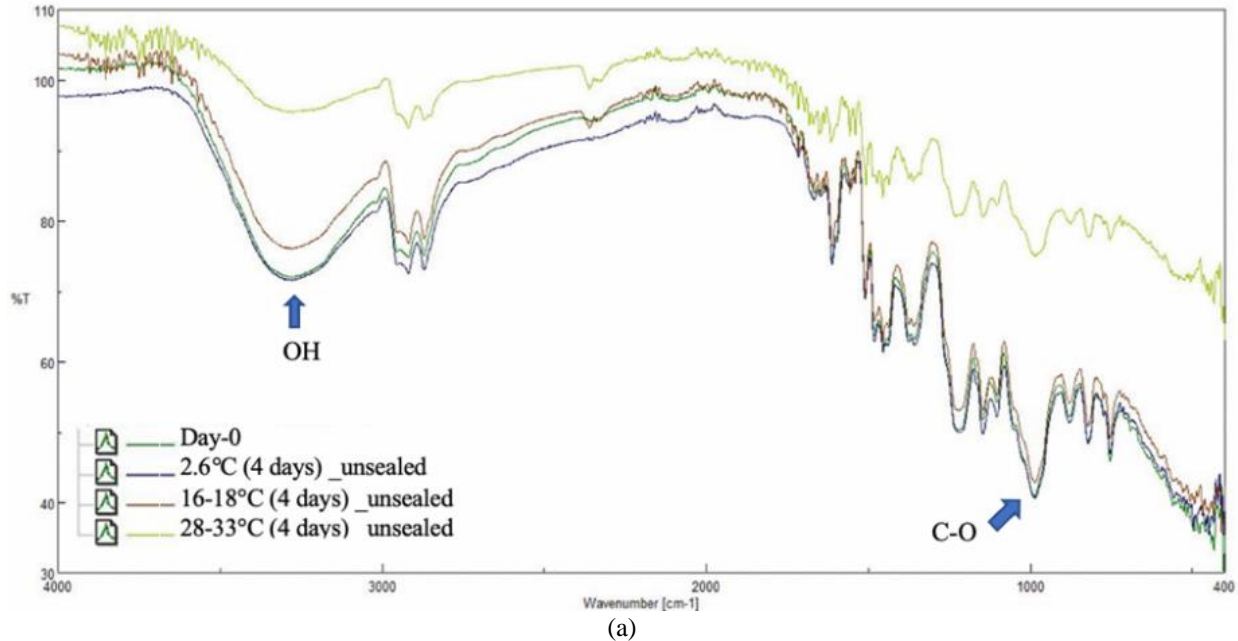
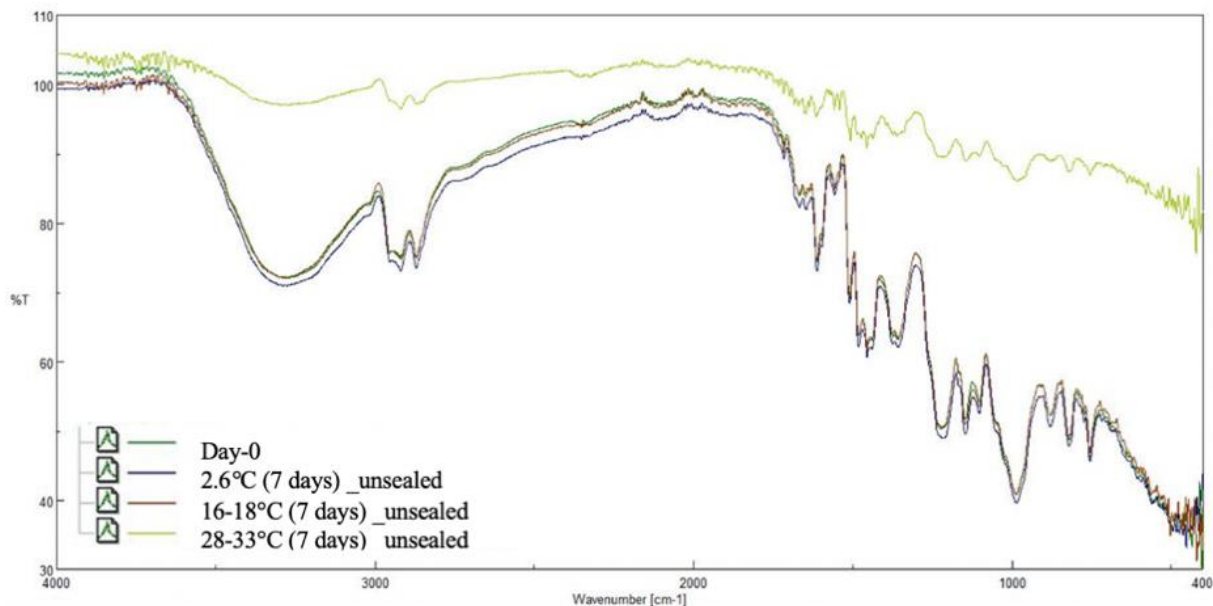


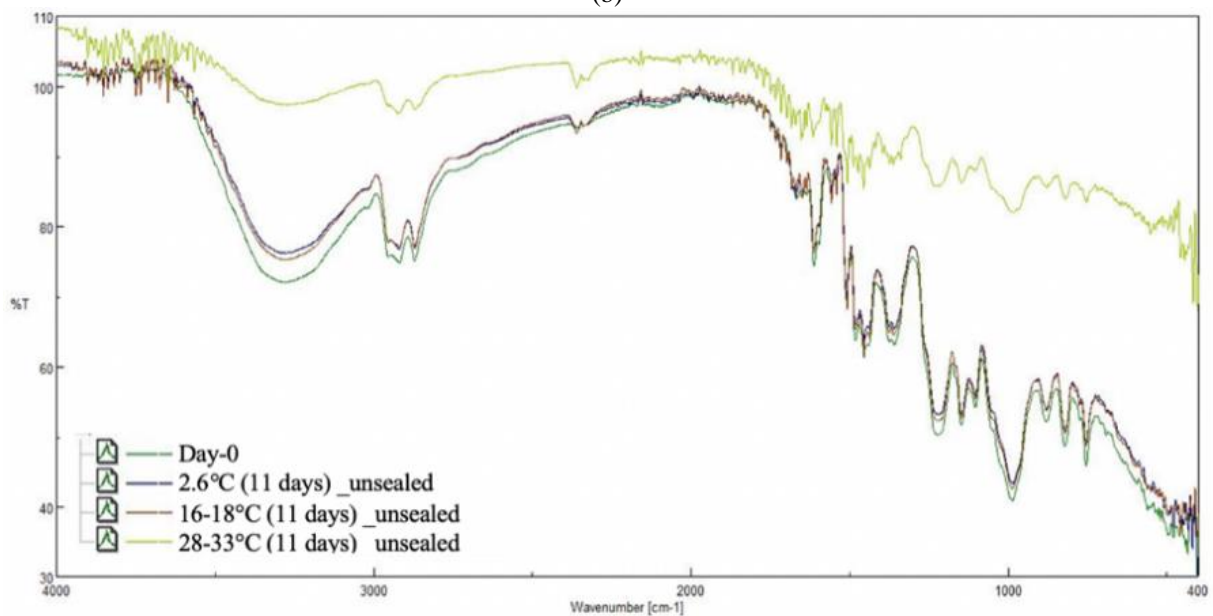
Figure 11. FTIR spectra of prepreg samples after different storage periods: 4 days (a), 7 days (b), and 11 days (c) in sealed condition. There were no discernable changes evident on the percent transmittance of the FTIR spectra between 2.6°C and 16-18°C. However, the FTIR spectra of prepreg samples stored at 28-33°C showed significant decrease in percent transmittance of important functional groups.

Comparable with the sealed condition, percent transmittance of volatiles in the prepreg samples decreased drastically upon simulated storage at 28-33 °C under the unsealed condition (Figure 12).





(b)



(c)

Figure 12. The FTIR spectra of prepreg samples showed a significant decrease in percent transmittance of alcohol and ketone functional groups for ET unsealed condition when compared to both FT and ET unsealed conditions. This trend was evident in the overlaying FTIR spectra after 4 days (a), 7 days (b), and 11 days (c) of simulated storage.

Two summary plots of percent transmittance of alcohol groups ($3200\text{--}3550\text{ cm}^{-1}$) and etheric bonds (1000 cm^{-1}) were constructed for the sealed condition. At low storage temperature ranges, the percent transmittance of etheric bonds remained constant on day 4 and day 7. On day 11, the percent transmittance of etheric bonds increased slightly at low storage temperatures. However, the percent transmittance of etheric bonds increased remarkably upon simulated storage at $28\text{--}33^\circ\text{C}$. Likewise, the percent transmittance of alcohol groups was close to 100%,

implying significant loss of alcohol groups after 4 days of storage at 28-33°C. For low-temperature storages, the percent transmittance of alcohol groups remained relatively constant, except for a small decrease on day 7 (Figure 13).

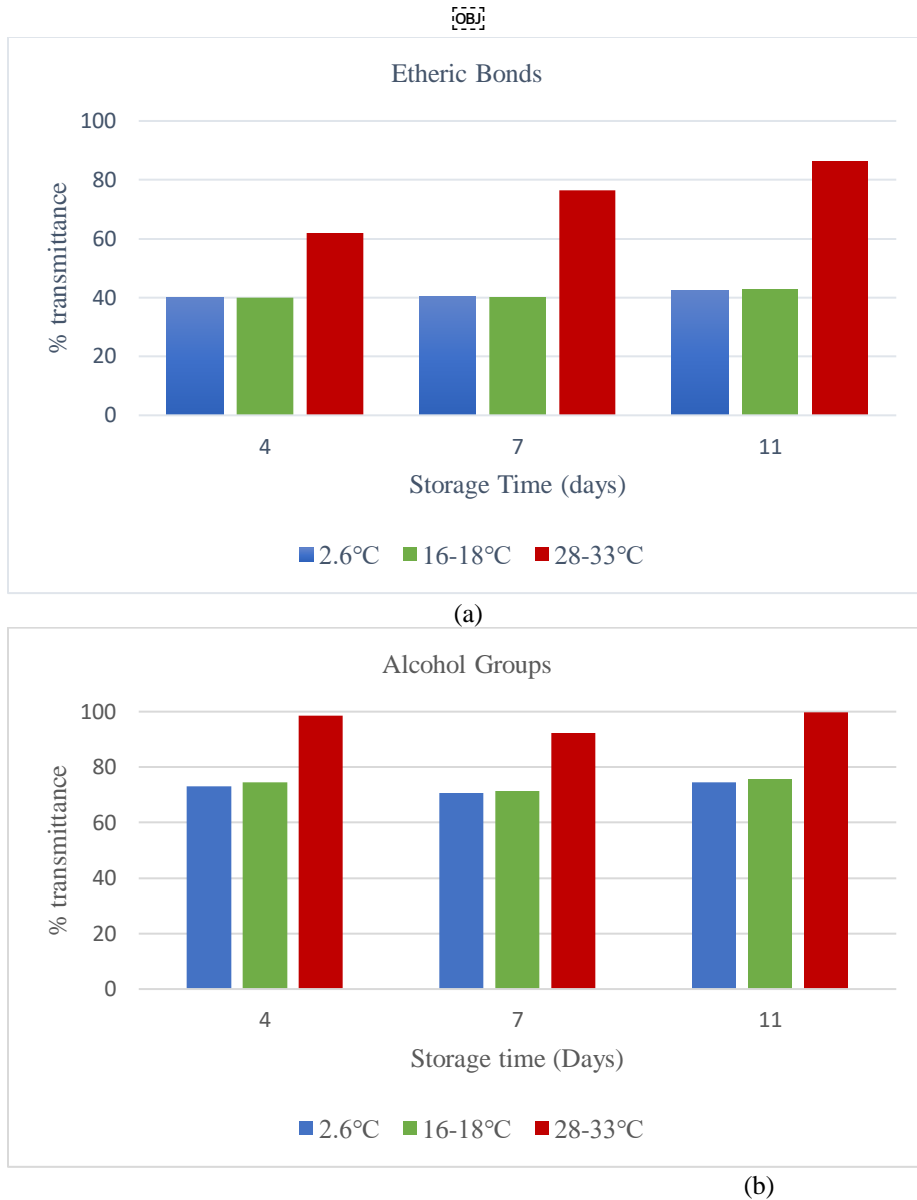


Figure 13. Transmittance change of etheric bonds (a) and alcohol groups (b) throughout storages showed significant volatiles loss at elevated storage temperatures (28-33°C).

TGA Results

The presence of remaining volatiles in prepregs were compared as weight loss in percentage on TGA curves at 120°C, which is the curing temperature of phenolic resin. Note that a small change in weight loss represented a small weight loss in the remaining volatiles of the

prepreg after simulated storages. In the same manner, a higher weight loss of prepreg connoted that more volatiles content was remained in the prepregs upon storage. A trend in a similar way to the trend seen on the FTIR results was shown on the TGA data of prepregs (Figure 14).

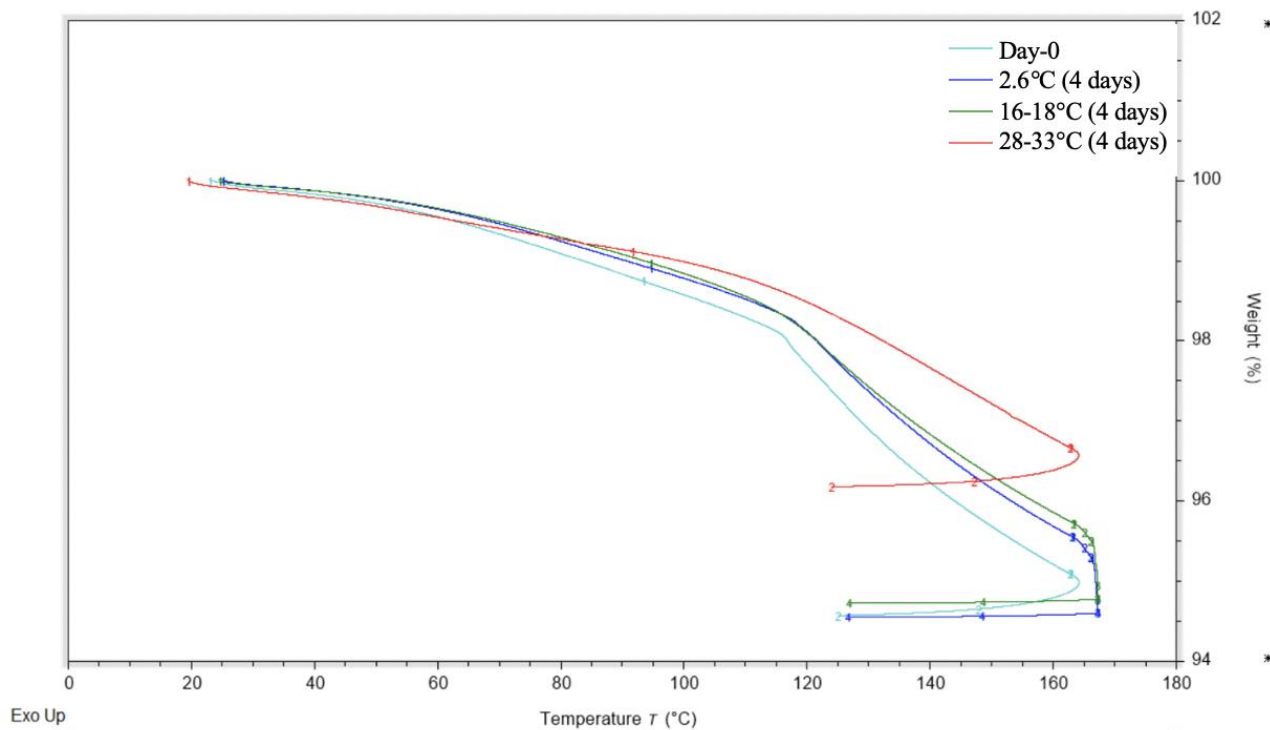
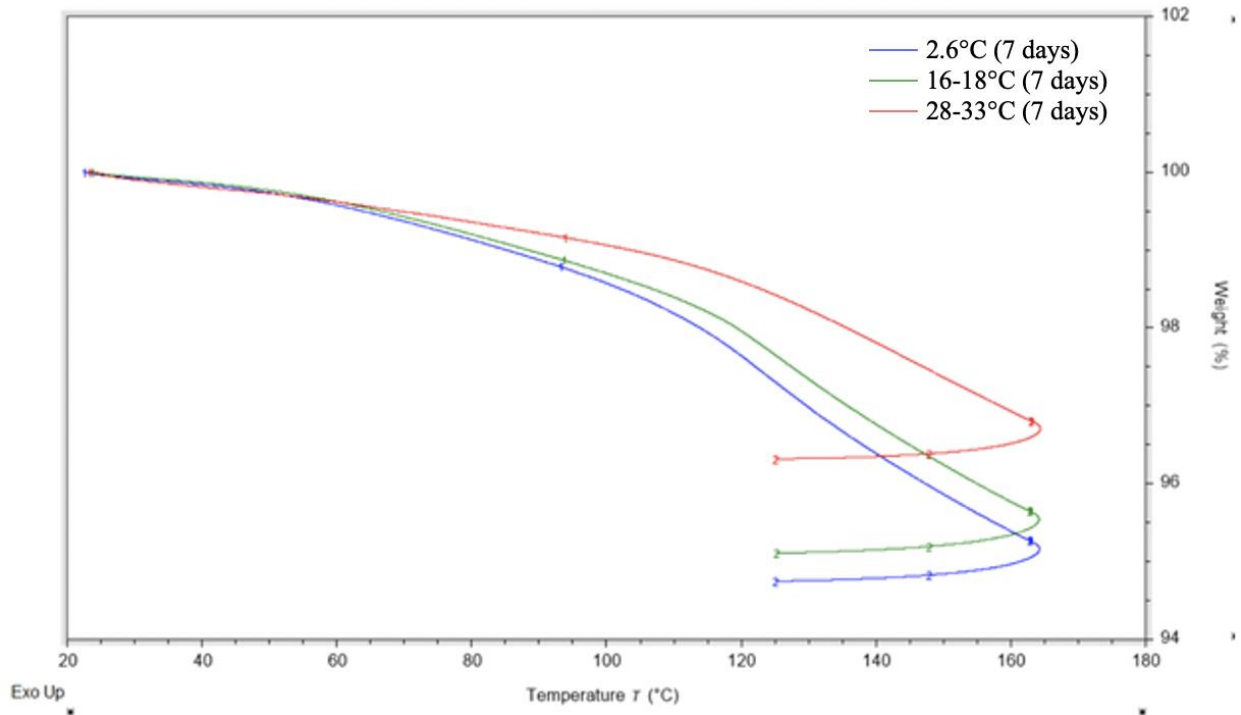
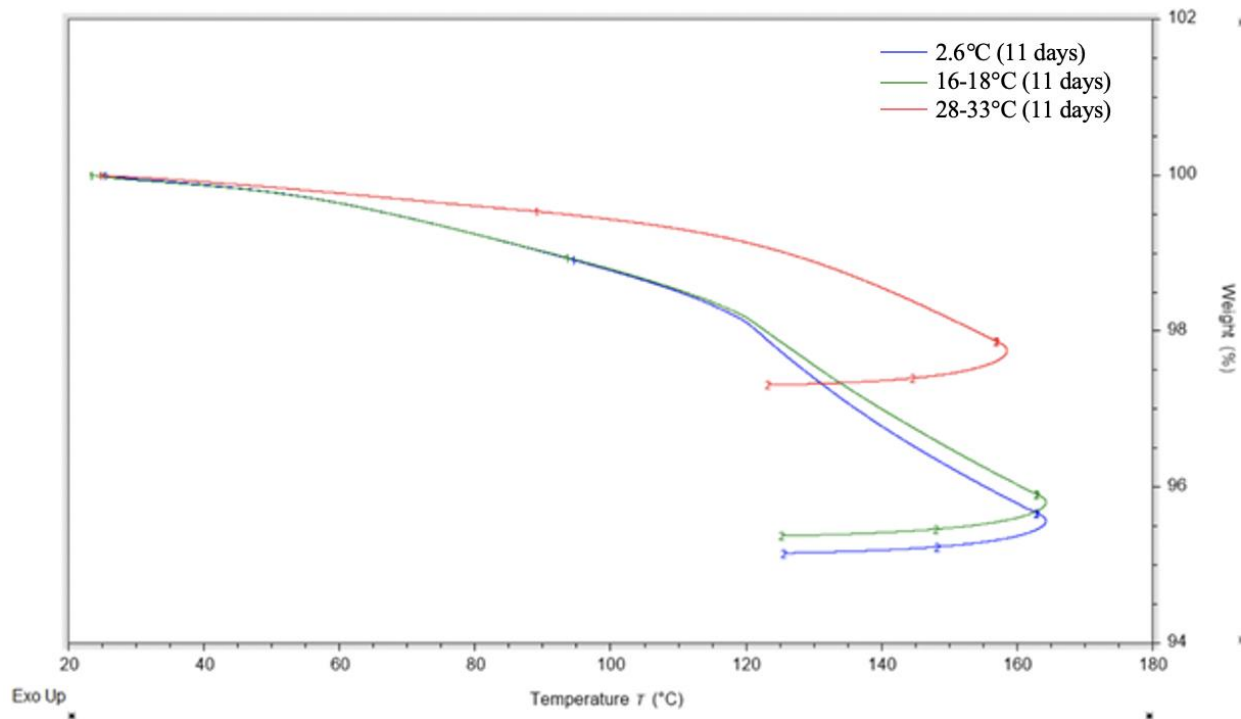


Figure 14. A comparison of TGA data from day 4 of storage for sealed samples stored at 2.6°C, 16-18°C, and 28-33°C.

As expected, there was no discernible difference in weight loss of volatiles between samples stored at 2.6°C and 16-18°C after 4 days of simulated storage. However, the loss of volatiles at storage temperatures of 28-33°C was noticeable when compared to volatiles loss of prepregs during low temperature storages at 2.6°C and 16-18°C. The TGA curve of day-0 sample was used as a reference in comparison to volatiles loss during all simulated storages. The weight loss of remaining volatiles decreased with increasing storage temperature showed on the overlaid TGA curves on day-7 and day-11 (Figure 15).



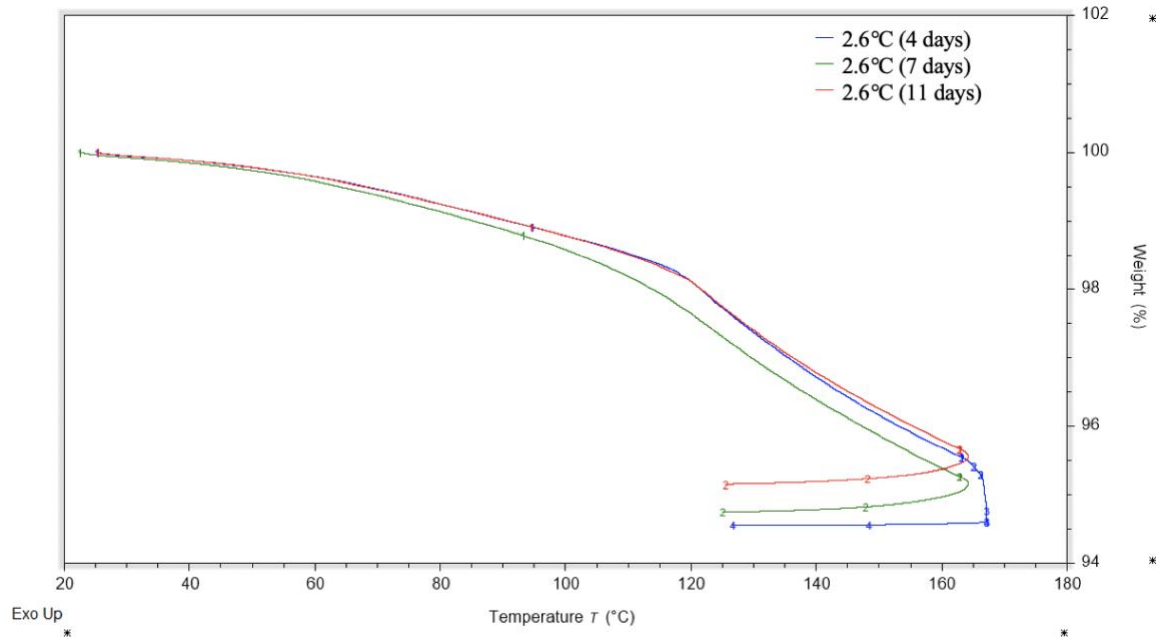
(a)



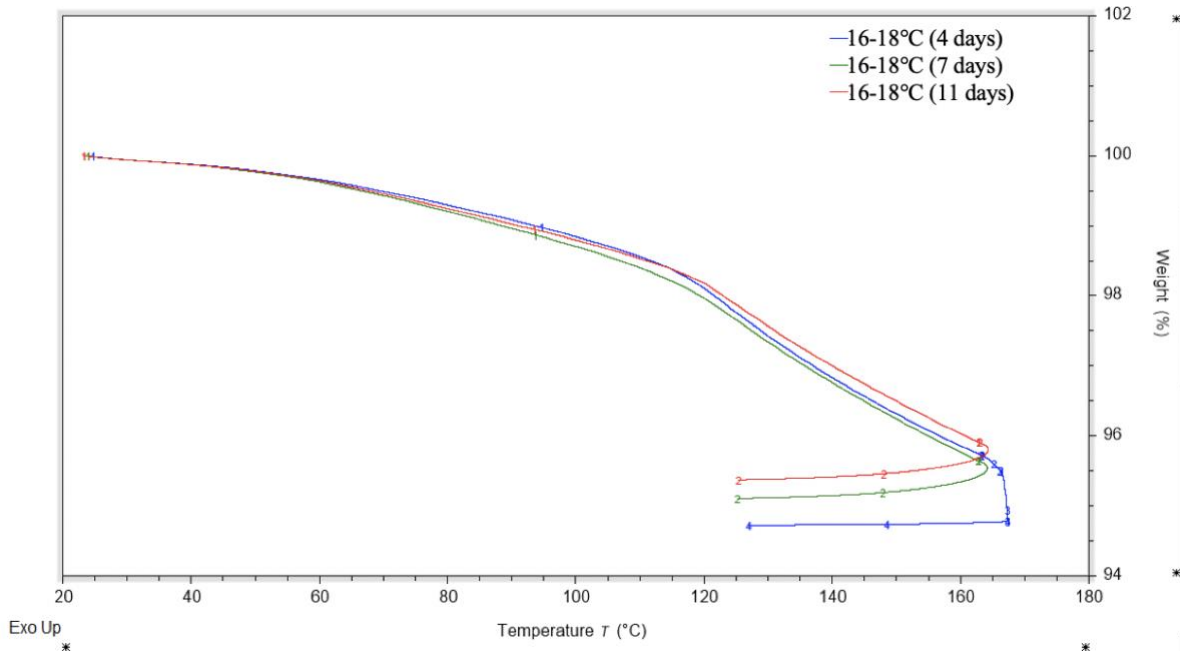
(b)

Figure 15. Overlaying TGA curves of prepreg samples after 7 days (a) and 11 days (b) of simulated storages at 2.6°C, 16-18°C, and 28-33°C.

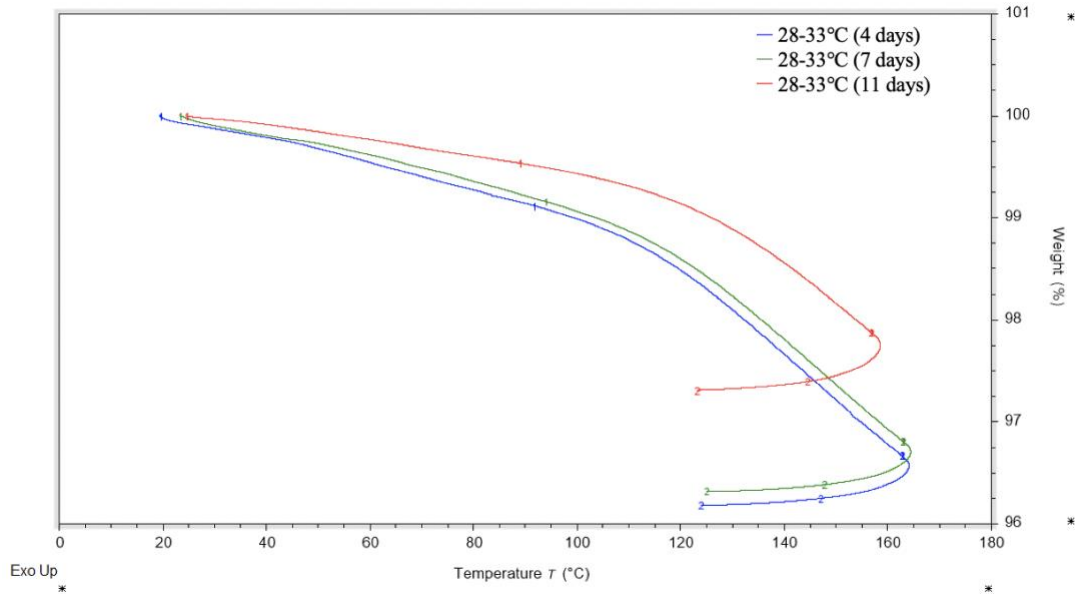
Overlaid TGA curves of preregs upon simulated storages at 2.6°C, 16-18°C, and 28-33°C throughout the 11 days showed weight loss of remaining volatiles decreased with a longer storage period (Figure 16).



(a)



(b)



(c)

Figure 16. Comparison TGA curves of prepreg samples stored at 2.6°C, 16-18°C, and 28-33°C throughout different storage length showing similar weight loss (%) of volatiles at 120°C on both day 4 and day 7 at temperature ranges of 2.6°C and 16-18°C.

To better compared the volatiles loss during simulated storages, the weight loss of remaining volatiles of prepreg throughout different storage lengths and storage temperature ranges were compared at the curing temperature (120°C) of phenolic resin. The weight loss of remaining volatiles of prepregs at low temperature storages was greater as compared to the weight loss of remaining volatiles at 28-33°C. Noticeable increase in weight loss of volatiles was detected by TGA on day 7 of low temperature storages at 2.6°C and 16-18°C. This could be a result of moisture absorption of prepregs during storage. Moreover, although the weight loss of remaining volatiles decreased as the storage length increased, the decrease in weight loss of volatiles caused by the elevated storage temperature was more prominent (Figure 17).

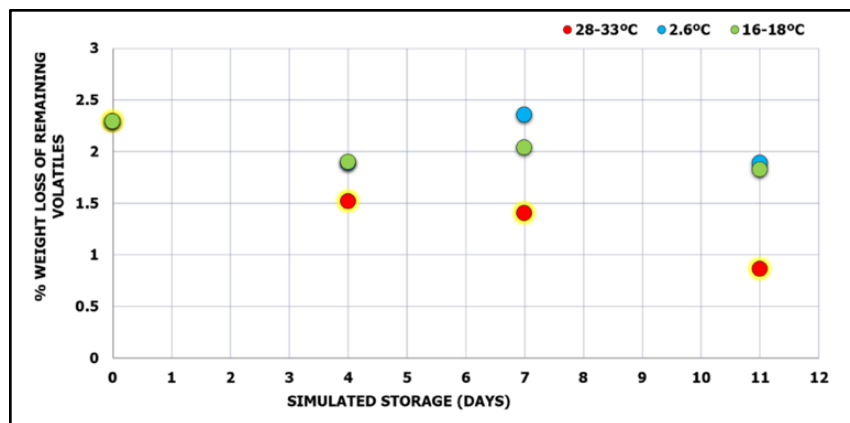


Figure 17. A comparison chart of TGA results of prepregs throughout storages at different temperatures. Data points extracted from TGA curves of samples at 120°C showing the loss of most volatiles occurred in simulated storage at 28-33°C.

Discussion

The lower ambient temperature does not cause a great loss of volatiles when comparing the results of the 2.6°C and 16-18°C storages. Results from physical observations on prepreg indicated the 28-33°C simulated out-time lost most of its original flexibility and tackiness after day 7.

Throughout 11 days, FTIR data from low-temperature storages were close to identical, indicating that prepreg in the lower ambient temperature and company storage temperature experienced a similar loss of volatiles. However, when the storage temperature was at 28-33 °C, the peak intensity of the detected functional groups, including the key volatiles, decreased significantly. As the peak intensity decreased, the percent transmittance of detected volatiles increased, meaning less bond population of volatiles was detected. Because the phenolic resin type in the prepreg sample is a resole resin, methylene (or ether) bridges are generated between hydroxyl methylene phenols from a condensation reaction at elevated temperatures. In other words, the formation process of methylene (or ether) bridging is the curing process of the prepreg. Therefore, the intensity of the peak at 1000 cm⁻¹ on the FTIR spectra is critical to monitor the curing of prepreg samples during simulated storages. Additionally, the decreasing peak around 1000 cm⁻¹ (C-O) for the prepreg stored at 28-33°C indicated that the prepreg experienced curing as methylene (or ether) bridging occurred through the elimination of hydroxyl (OH) groups from the etheric bonds. Furthermore, the percent transmittance of alcohol groups increased significantly and quickly upon storages, implying the unsealed condition drove off the volatiles at 28-33C as compared to the sealed condition.

The weight loss of volatiles on TGA results were compared at 120°C to investigate the volatiles loss during simulated storages. A higher weight loss value represents a higher amount of remaining volatiles in the prepreg after storage. As seen from the TGA results, a larger decrease in the remaining volatiles was observed at 28-33°C when the comparison was made between different storage temperature ranges. However, the decrease in weight loss of remaining volatiles was less prominent when the comparison was made between different storage lengths.

It should be mentioned that the percent transmittance of alcohol groups decreased on FTIR results of day-7 samples stored at 2.6°C and 16-18°C. The decreased in percent transmittance of alcohol groups represented an increase in the detected bond population of alcohols. This could be a result of water absorption upon low-temperature storages as the percent transmittance of etheric groups did not change on day 7. The constant percent transmittance of etheric groups indicated the absence of curing of the prepreg at low storage temperatures. Similarly, a noticeable increase in the weight loss of remaining volatiles was evident on day 7 of the TGA comparison data. Due to the comparison on the TGA data was made at 120°C, which was above the boiling point of water, the increasing weight loss of remaining volatiles on day 7 for low-temperature storages could be a result of moisture absorption of the prepreg during storage.

Conclusions

The elevated storage temperature has a greater effect on the loss of volatiles in the prepreg compared to the length of storage. Additionally, the percent transmittance of etheric bonds on the FTIR spectra was used to monitor the curing of prepreg samples throughout storages. Noticeable curing progression of prepreg was observed on the FTIR results of samples upon simulated storage at 28-33°C. As concluded from both FTIR and TGA results, the most loss of volatiles occurred at 28-33°C. Lastly, loss of volatiles in the prepreg occurred quickly at 28-33°C under unsealed condition.

Recommendations

As the experiment results suggested, it is recommended that there be a low-temperature controlled environment provided during transport and for prepreg to be stored in low-temperature storage on hot summer days. Along with it, it is recommended that the prepreg is kept in a seal bag during transit and storage to maintain the best condition.

References

- [1] P.L. Mallick, *Reinforced Composites Materials, Manufacturing, and Design*, 3rd ed. Dearborn, Michigan: CRC Press Taylor and Francis Group, 2007.
- [2] S. Qureshi, "Phenolic Resins," in *ASM Handbook*, vol. 21, ASM International, 2001.
- [3] Polymerdatabase.com. 2021. *Properties of Phenoplasts*. [online] Available at: <<https://polymerdatabase.com>> [Accessed 3 November 2020].
- [4] L. Uyigue, "Estimation of Product Yield and Kinetic Parameters of Phenolic-Resin Pre-Polymer Synthesis Using Acid and Base as Catalyst", *International Journal of Engineering and Modern Technology*, vol. 4, no. 3, p. 30, 2018. Available: <http://www.iiardpub.org>. [Accessed 4 June 2021].
- [5] PELIN, G., PELIN, C., ŞTEFAN, A., DINCĂ, I., FICAI, A., ANDRONESCU, E. and TRUŞCĂ, R., 2016. Influence of nanometric silicon carbide on phenolic resin composites properties. *Bulletin of Materials Science*, [online] 39(3), pp.769-775. Available at: <<https://www.researchgate.net/publication/303781622>> [Accessed 31 January 2021].
- [6] SigmaAldrich.com. 2021. *IR Spectrum Taby and Chart*. [online] Available at: <<https://www.sigmaaldrich.com/technical-documents/articles/biology/ir-spectrum-table.html>> [Accessed 4 February 2021].
- [7] Souza, W., Garcia, K., Von Dollinger, C. and Pardini, L., 2015. Electrical Behavior of Carbon Fiber/Phenolic Composite during Pyrolysis. *Materials Research*, [online] 18(6), pp.1209-1216. Available at <<https://www.researchgate.net/publication/283620970>> [Accessed 3 February 2021].
- [8] "Thermoset Prepreg Systems - Litzler," *Litzler Co.* <https://www.calitzler.com/prepreg-systems/thermoset-prepreg-systems/> (accessed Nov. 06, 2020).
- [9] P.L. Mallick, *Reinforced Composites Materials, Manufacturing, and Design*, 3rd ed. Dearborn, Michigan: CRC Press Taylor and Francis Group, 2007.
- [10] "Engineered Materials," *Safran Cabin*. <https://www.safran-cabin.com/structures/engineered-materials-1> (accessed Nov. 07, 2020).
- [11] Safran Cabin. 2021. *Overhead Bins and Liners*. [online] Available at: <<https://www.safran-cabin.com/floor-floor/overhead-bins-and-liners-0>> [Accessed 3 February 2021].
- [12] J. Monni, L. Alvila, and T. Pakkanen, "Structural and Physical Changes in Phenol-Formaldehyde Resol Resin, as a Function of the Degree of Condensation of the Resol Solution," *Industrial & Engineering Chemistry Research*, vol. 46, no. 21, pp. 6916-6924, 2007.
- [13] ASTM Standard E12525-98, 2013, " Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis," ASTM International, West Conshohocken, PA, 2013, DOI: 10.1520/E1252-98R13, www.astm.org.
- [14] ASTM Standard D3530-20, 2020, "Standard Test Method for Volatiles Content of Composite Material Prepreg