UNIVERSITI PUTRA MALAYSIA

THE EFFECT OF THERMO-OXIDATIVE AGING ON PROPERTIES OF EGLASS FIBER-REINFORCED EPOXY COMPOSITES

AMIN KHAJEH

THE EFFECT OF THERMO-OXIDATIVE AGING ON PROPERTIES OF E-GLASS FIBER-REINFORCED EPOXY COMPOSITES

By

AMIN KHAJEH

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

May 2016

DEDICATION

To my beloved parents

For their

Love

Endless support

&

Encouragement

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Science

THE EFFECT OF THERMO-OXIDATIVE AGING ON PROPERTIES OF E-GLASS FIBER-REINFORCED EPOXY COMPOSITES

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May 2016

Chairman : Faizal Bin Mustapha, PhD, PEng
Faculty : Engineering

The present study aims to investigate the effect of thermo-oxidative aging on the mechanical, chemical, physical properties of EHG250-68-37 E-glass fiber-reinforced epoxy preimpregnated.

To achieve the proposed research objectives, laminates of EHG-68-37 fiberglass/epoxy prepreg were exposed 800 h in isothermal condition and air-circulating oven at 82 °C. It is noteworthy that, before aging, specimens were dried to constant weight under vacuum at 70 °C in accordance with ASTM D 5229/D 5229M due to hydrophilic matrix. The variations of mechanical properties (the elastic moduli, tensile strength, strain break, and toughness) were quantified by conducting tensile tests on both aged and un-aged specimens based on ASTM D3039. Chemical changes in composites due to thermo-oxidative aging were analyzed by, Dynamic mechanical analysis (DMA), Differential Scanning Calorimetry (DSC), and Fourier Transform Infrared spectroscopy (FTIR). Physical degradation mechanisms resulting from sub-T_g aging were monitored by weight loss measurements as a function of time and Scanning Electron Microscope (SEM) to investigate superficial resin, cross sectional, and the cryofractured surface morphology.

The showed the toughness, tensile strength and modulus of the composites were increased after pronounced aging conditions, 3.7%, 48%, and 59%, respectively. Whereas a decrease (0.22%) was observed in the strain break. DMA results revealed that the glass transition temperature and rubbery state modulus were increased as a result of the matrix densification. FTIR spectroscopy demonstrated the formation of carbonyl compounds around IR band 1735 cm^{-1} due to oxidation of the chemical structure of the aromatic ethers. SEM observations indicated the existence of minor superficial cracking, growth in size and number of voids, and poor fiber-matrix adhesion after aging. In addition, a minor mass change was observed from mass loss monitoring methods. The overall findings suggest that post-curing and oxidation enhanced the brittleness of the resin, leading to a significant decline in the useful structural life of the thin-skinned composite.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

KESAN PENUAAN TERMO-OKSIDATIF TERHADAP SIFAT-SIFAT KOMPOSIT EPOKSI DIPERKUKUH GENTIAN KACA-E

Oleh

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Kajian ini bertujuan untuk mengkaji kesan penuaan termal-oksidatif pada sifat mekanikal, kimia, fizikal EHG250-68-37 gentian kaca-E bertetulang pracampuran epoksi. Untuk mencapai objektif kajian yang dicadangkan, lamina daripada EHG-68-37 gentian kaca / pracampuran epoksi didedahkan dalam keadaan isoterma dan ketuhar pada suhu 82°C selama 800jam. Perlu diperhatikan bahawa, sebelum penuaan, spesimen telah dikeringkan pada satu jisim kekal dibawah vakum pada suhu 70°C mengikut ASTM D 5229 / D 5229M kerana matriks bersifat hidrofilik. Kepelbagaian sifat mekanik (modulus elastik, kekuatan tegangan, titik putus terikan, dan keliatan) telah diukur dengan menjalankan ujian tegangan di kedua-dua spesimen yang melalui proses penuaan dan tidak melalui proses penuaan berdasarkan ASTM D3039. Perubahan kimia dalam komposit disebabkan oleh penuaan termal-oksidatif dianalisis mengunakan Analisis Mekanikal Dinamik (DMA), Differential Scanning Calorimetry (DSC), dan Jelmaan Fourier Spektroskopi Inframerah (FTIR). Mekanisme kemusnahan fizikal yang disebabkan oleh Sub-Tg penuaan dipantau berdasarkan pengurangan berat terhadap masa dan Mikroskop Imbasan Elektron (SEM) untuk menganalisis keadaan permukaan resin, keratan rentas, dan permukaan morfologi cryofractured. Itu menunjukkan kekuatan, kekuatan tegangan dan modulus bagi komposit meningkat, masing-masing sebanyak 3.7%, 48%, dan 59%. Manakala penurunan (0.22%) diperhatikan pada titik putus terikan. Keputusan DMA mendedahkan bahawa suhu peralihan kaca dan modulus elastik telah meningkat akibat pemadatan matriks. FTIR spektroskop pembentukan sebatian karbonil sekitar band IR 1735cm^{-1} kerana pengoksidaan struktur kimia eter aromatik. Pemerhatian SEM menunjukkan adanya keretakan kecil pada permukaan, pertumbuhan saiz dan bilangan lubang, dan sedikit gentian-matriks selepas penuaan. Di samping itu, melalui kaedah pemantauan kehilangan jisim, jisim mengalami sedikit perubahan. Hasil kajian menunjukkan bahawa pengawetan dan pengoksidaan telah meningkatkan kerapuhan resin, yang membawa kepada penurunan yang ketara dalam kitaran penggunaan struktur komposit nipis
.

ACKNOWLEDGEMENTS

The author wishes to express his cordial thanks to his academic supervisor, Associate Professor Faizal bin Mustapha (University Putra Malaysia) and Professor György Bánhegyi (Scientific advisor in Medicontur Ltd., Szeged, Polymer Laboratory), which due to their helpful supervision, wise suggestions, constructive advice, understanding, and encouragement made this research work possible.

The author is grateful to his supervisory committee members and senior lecturer, Dr. Dayang Laila Bt. Abang Haji Abdul Majid, Dr. Noorfaizal Yidris, and Mohamed Thariq Hameed Sultan from the Aerospace Department for their overall support and dedication to the project.

Gratitude is also expressed to Mrs. Nor Hasni Binti Zahari from the department of Chemical and Environmental Engineering (UPM) for her able help in the laboratory.

Finally, the author would like also to extend his appreciation to Meysam Toozandehjani, Noor Hazira Binti Mohamed Haidzir, Hossein Mojadadi, Farhad Ostovan, , and Saman Azhari for helpful and practical discussions in developing thesis concepts.

I certify that a Thesis Examination Committee has met on 18 May 2016 to conduct the final examination of Amin Khajeh on his thesis entitled "Effect of Thermo-Oxidative Aging on Properties of E-Glass Fibre-Reinforced Epoxy Composites" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABBREVIATIONS

G_I^C	Critical energy release rate/ fracture toughness at Mode I
O_2	Oxygen molecule
$P^{\cdot}$	Free radical molecule
$POO^{\cdot}$	Peroxide radical
1,3-BAC	1,3-bisaminomethylcyclohexane
ASTM	American Society for Testing and Materials
BMI	Bismalemide
CFRP	Carbon fiber reinforced plastic
CGMCs	Carbon and graphic matrix composites
CIM	Confocal interferometric microscopy
CMCs	Ceramic-matrix composites
CNC	Computer Numerical Control
C_p	Heat capacity in constant pressure
DGEBA	Diglycidyl ether of bisphenol-A
DMA	Dynamic Mechanical Analysis
DSC	Differential scanning calorimetry
E'	Storage modulus
E"	Loss modulus
EDX	Energy-dispersive X-ray
EPN	Epoxy Phenol Novolac
FTIR	Fourier transform infrared spectroscopy
GFRPs	Glass fiber reinforced plastics
ITX	Isopropylthioxanthone
KBr	Potassium Bromide
LMPA	Low molecular polyamide
MMCs	Metal matrix composites
MTHPA	Methyl tetra hydro phthalic anhydride
OMCs	Organic-matrix composites
PAA	Polyamideoamine
PEEK	Poly-ether-ether-ketone
PEI	Poly –ether-imide
PEKK	Poly-ether-ketone-ketone
PMCs	Polymer matrix composites
POPA	Polyoxyproylene
SEM	Scanning electron microscopy
SiC	Silicon Carbide
Tan δ	Mechanical damping; Tan $\delta = {E"}/{E'}$
TEPA	Tetraethylenepentamine
T_g	Glass transition temperature
TMA	Thermal mechanical analysis

CHAPTER 1

INTRODUCTION

In the chapter, the background of the study, statement of the problem, research objectives, research scope and significance of the research study to the researcher and engineering community are covered.

1.1 Research background

There has been sustained interest on PMCs (Polymer Matrix Composites) from a wide range of specialists especially in recent decades. Initially, the application of composites in the military sparked their commercial usage that began after World War II. New landscape pressures couple with the energy crisis experienced in the 1970s prompted military and commercial aircraft manufacturers to employ the lightweight composite structures. Furthermore, the advancements achieved in the composite area have permitted considerable decrements of weight in the structural design. In comparison to the metal alloys, composites are superior in regard to stiffness and strength to weight ratio, corrosion resistance and outstanding fatigue properties.

Even though the exhibit desirable mechanical properties and low density, concerns arise over the overall and long-term durability that polymer matrix composites have, especially in relation to the load bearing to sustain performance under increased temperatures. Generally, elevated temperatures are likely to cause reversible changes, that is, physical aging, and the non-reversible changes, that is, chemical aging, to be experienced in PMCs. Particularly, combining elevated temperatures and oxygen-induced non-reversible changes is likely to result in considerable decrease in properties. Such non-reversible variances are commonly called ‘thermo-oxidative aging’ and oxygen diffusion into the composite initiates them.

Numerous research works have been revealed that thermal oxidative aging may change the chemical structure of polymer matrix composites. Alterations to the chemical structure during thermo-oxidative degradation include post-curing [1-11], loss of volatiles [12-17], dehydration [4, 18, 19], chain scission [15, 20-24], additional crosslinking [2, 4], and carbonyl growth [8, 19]. The initial chemical changes are accompanied by dehydration of secondary alcohols and the release low molecular weight gaseous species due to random chain scission. However, at moderate heat exposures (24℃ – 177℃), chain crosslinking is the dominant chemical change in the matrix compared to chain scission [25]. Indeed, the increase in the crosslink density of the cured matrix primarily occurs during the initial aging period and are caused by post-cure reactions [4, 6, 26, 27], which result in the excessive brittleness in the matrix [28]. As aging proceeds in the presence of oxygen, susceptible chemical structures in the resin are oxidized to various carbonyl containing groups. Therefore, matrix embrittlement increases with the oxygen concentration and aging time [12, 29]. Extensive research efforts have revealed that the matrix embrittlement enhance bulk mechanical properties such as tensile strength and modulus [30-32] and toughness [33, 34]. However, some studies observed a reduction in toughness resulted from the brittleness in the matrix [35, 36]. According to Colin et al. [37], changes observed in the bulk characteristics of the polymer matrix are caused by the superficial oxidized layer forming as a result of liberated segments volatile being oxidized in the thermo-oxidative aging phase [38-41]. On establishing this, numerous comprehensive research efforts were undertaken on polymer matrix material for investigating the brittle attributes that the matrix exhibit through the thickness. The findings of these studies showed that the matrix embrittlement is confined to the superficial layers and the core of the matrix remained intact [13, 38, 42, 43].

1.2 Problem Statement

Oxidation takes place only in the superficial layers of composites due to their exposure to aging while core of the aged composites mostly remain intact. Considering the advent in applying thin-skinned composite of approximately 1-6 mm in thickness in aeronautical structure, it becomes necessary to ask whether relying on specimen thickness in characterizing bulk attributes in evaluating durability would be an issue. Considering this, Tsotsis [44] remarked that using specimens that are too thick will delay the onset of observable changes in many properties because may be sufficient unchanged material to carry mechanical loads, such that loss or reduction in properties of a material's outer layers masks the degradation. Cinquin and Medda [45] studied the influence of laminate thickness on composite durability for long term. They conducted a durability evaluation on carbon/epoxy laminate with 5.15 mm and 26 mm thick over period of 30,000 h and at temperature of 150°C. The findings of the study indicated that the residual mechanical properties are more affected on thin composite than on thick composites.

In the context of "durability", there is an aspect of both physic-chemical and mechanical effects determining the life time of the considered composite materials [46]. Thus, it is necessary that the thin-skinned composites be characterized on the constitutional level to be able to understand their chemical, mechanical and physical responses caused by thermo-oxidative processes. Nevertheless, the investigation hereby undertaken to evaluate the durability of the thin-skinned composites focused on measuring weight loss and mechanical characterization. Furthermore, even though the usage of the woven fiberglass/epoxy prepreg composites that are thin-skinned has continued rising, the thin-skinned composite remain under-researched when it comes to its durability when subjected to thermo-oxidative aging scenario. Therefore, the primary aim of conducting this thesis was to examine how thermo-oxidative aging affect the durability of the woven fiberglass/epoxy prepreg composites with a thin skin in relation to the physical, chemical and mechanical aspects and in establishing the origin of in-service failure that arise prematurely.

1.3 Research Objectives

This study mainly seeks to examine the influence that thermo-oxidative aging has on the durability of the EHG250-68-37 woven fiberglass/epoxy prepreg as well as the resultant effect on the mechanical attributes, physical structures and chemical structures. It is possible to split the evaluation of durability into three objectives:

1. To determine the mechanical degradation (e.g. toughness, tensile strength and modulus) of both un-aged and aged samples by tensile test.
2. To evaluate chemical degradation in the matrix induced by thermo-oxidative aging by dynamic mechanical analysis, differential scanning calorimetry, and Fourier transform infrared spectroscopy tests.
3. To verify physical degradation in the both un-aged and aged composites resulting from pronounced aging by weight loss and micrographic observations of topmost, cross sectional, and cryofractured surface.

1.4 Scopes of Work

The thesis will evaluate the influence that thermo-oxidative degradation has on the durability of epoxy composite that is reinforced by fiberglass from chemical, mechanical and physical points of view. The current work aims at linking the premature alterations that take place in the thin-skinned composite panel with reduction in durability. The examination of thermal-oxidative degradation through principles-based dimension taking into account the thickness of the original composite assists in the assessment of the real toughness behavior applicable in use-condition through mechanical testing. Consequently, assessment of toughness value through the calculation of the area that is below the stress-strain curve approach was employed over the Charpy impact test because of the sub-size thickness of the available materials. Additionally, the thesis introduces a methodology on the basis of industrial interest, as the thermo-oxidative aging of the thin-skinned composites remains under-researched. Thus, the study is expected to add to the existing literature on the materials employed in manufacturing aircrafts particularly in regard to their durability in relation to the marked thermal-oxidative degradation.

1.5 Limitations

The main challenge in conducting the research likely to have limited the extent that FTIR and thermal analyses would cover relates to the failure by the manufacturers to reveal the compositional data and chemical structure of the matrix.

1.6 Research Contribution

The finding of this research work will redound to add to the existing literature on the EHG250-68-37 woven fiberglass/epoxy prepreg employed in manufacturing aircrafts particularly in regard to their thermal-oxidative degradation. In addition, the introduced methodology in this study will determine that which one of the physical aging and chemical aging has major role in the matrix embrittlement at the initial stage of thermo-oxidative aging (post curing period).This in turn, assists thin-skinned polymer matrix composite manufacturers to take into account a proper curing schedule for PMCs laminates to avoid premature in-service failures.

1.7 Thesis Organization

In this thesis, Chapter 2 will provide the literature review covering the relevant published articles on the isothermal thermo-oxidative aging on the polymer matrix composites as well as the consequent physical, mechanical and chemical variations. Whereas, Chapter 3 presents the experimental methodology employed in evaluating the durability of the thin-sinned composites. On its part, Chapter 4 provides the results that the experimental tests and discussions obtained. Eventually, Chapter 5 provides the conclusions and recommendations that can be drawn from the undertaken research.

REFERENCES

[1] Wang, Y., et al., *Accelerated Ageing Tests for Evaluations of a Durability Performance of Glass-fiber Reinforcement Polyester Composites.* J Mater Sci Technol, 2010. **26**(6): p. 572-576.

[2] Tsotsis, T.K., et al., *Aging of polymeric composite specimens for 5000 hours at elevated pressure and temperature.* Comp Sci Technol, 2001. **61**(1): p. 75-86.

[3] Carbas, R.J.C., et al., *Effect of post-cure on the glass transition temperature and mechanical properties of epoxy adhesives.* J Adhes Sci Technol, 2013. **27**(23): p. 2542-2557.

[4] Lv, X., et al., *Effect of thermal-oxidative aging on carbon fibre-bismaleimide composites.* Pigment Resin Technol, 2012. **41**(1): p. 34-41.

[5] Abrate, S., *Impact on Laminated Composites: Recent Advances.* Appl Mech Rev, 1994. **47**(11): p. 517-544.

[6] Bockenheimer, C., D. Fata, and W. Possart, *New aspects of aging in epoxy networks. I. Thermal aging.* J Appl Poly Sci, 2004. **91**(1): p. 361-368.

[7] Cherdoud-Chihani, A., M. Mouzali, and M.J.M. Abadie, *Study of crosslinking AMS/DGEBA system by FTIR.* J Appl Poly Sci, 1998. **69**(6): p. 1167-1178.

[8] Galant, C., et al., *Thermal and radio-oxidation of epoxy coatings.* Prog Org Coat, 2010. **69**(4): p. 322-329.

[9] Barral, L., et al., *Thermal degradation of a diglycidyl ether of bisphenol A/1,3-bisaminomethylcyclohexane (DGEBA/1,3-BAC) epoxy resin system.* Thermochimica Acta, 1995. **269–270**(0): p. 253-259.

[10] Pei, Y.M., et al., *Thermal-oxidative aging of DGEBA/EPN/LMPA epoxy system: Chemical structure and thermal-mechanical properties.* Poly Degrad Stabil, 2011. **96**(7): p. 1179-1186.

[11] Zahra, Y., et al., *Thermo-oxidative aging of epoxy coating systems.* Prog Org Coat, 2014. **77**(2): p. 380-387.

[12] Parvatareddy, H., et al., *Environmental aging of high-performance polymeric composites: Effects on durability.* Comp Sci Technol, 1995. **53**(4): p. 399-409.

[13] Bowles, K.J., D. Jayne, and T.A. Leonhardt, *Isothermal aging effects on PMR-15 resin.* S.A.M.P.E. quarterly, 1993. **24**(2): p. 2-9.

[14] Xiao, H.M., et al., *Microstructure evolution of SW/EPN composites during hot air aging.* J Appl Poly Sci, 2014. **131**(8).

[15] Decelle, J., N. Huet, and V. Bellenger, *Oxidation induced shrinkage for thermally aged epoxy networks.* Poly Degrad Stabil, 2003. **81**(2): p. 239-248.

[16] Colin, X. and J. Verdu, *Strategy for studying thermal oxidation of organic matrix composites.* Comp Sci Technol, 2005. **65**(3-4): p. 411-419.

[17] Ozcelik, O., L. Aktas, and M.C. Altan, *Thermo-oxidative degradation of graphite/epoxy composite laminates: Modeling and long-term predictions.* Exp Poly Lett, 2009. **3**(12): p. 797-803.

[18] Liu, Y.L., et al., *Novel thermosetting resins based on 4-(N-maleimido)phenylglycidylether: III. Studies on the thermal degradation kinetics and mechanisms of the cured resins.* Poly Degrad Stabil, 2004. **86**(1): p. 135-145.

[19] Mailhot, B., et al., *Study of the degradation of an epoxy/amine resin, 1 photo- and thermo-chemical mechanisms.* Macromol Chem Phys, 2005. **206**(5): p. 575-584.

[20] Chen, J.S., et al., *Controlled degradation of epoxy networks: Analysis of crosslink density and glass transition temperature changes in thermally reworkable thermosets.* Polymer, 2004. **45**(6): p. 1939-1950.

[21] Wolfrum, J., S. Eibl, and L. Lietch, *Rapid evaluation of long-term thermal degradation of carbon fibre epoxy composites.* Comp Sci Technol, 2009. **69**(3-4): p. 523-530.

[22] Awaja, F. and P.J. Pigram, *Surface molecular characterisation of different epoxy resin composites subjected to UV accelerated degradation using XPS and ToF-SIMS.* Poly Degrad Stabil, 2009. **94**(4): p. 651-658.

[23] Dyakonov, T., et al., *Thermal analysis of some aromatic amine cured model epoxy resin systems - II: Residues of degradation.* Poly Degrad Stabil, 1996. **54**(1): p. 67-83.

[24] Buch, X. and M.E.R. Shanahan, *Thermal and thermo-oxidative ageing of an epoxy adhesive.* Poly Degrad Stabil, 2000. **68**(3): p. 403-411.

[25] Gates, T.S. and M.A. Grayson, *On the use of accelerated aging methods for screening high temperature polymeric composite materials.* Collection of Technical Papers - AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference, 1999. **2**: p. 925-935.

[26] Li, K., et al., *The change of thermal-mechanical properties and chemical structure of ambient cured DGEBA/TEPA under accelerated thermo-oxidative aging.* Poly Degrad Stabil, 2013. **98**(11): p. 2340-2346.

[27] Akay, M. and G.R. Spratt, *Evaluation of thermal ageing of a carbon fibre reinforced bismalemide.* Comp Sci Technol, 2008. **68**(15–16): p. 3081-3086.

[28] Kumar, B.G., R.P. Singh, and T. Nakamura, *Degradation of Carbon Fiber-Reinforced Epoxy Composites by Ultraviolet Radiation and Condensation.* J Comp Mater, 2002. **36**(24): p. 2713-2733.

[29] Kelen, T., *Polymer degradation*. 1983: Van Nostrand Reinhold.

[30] Wang, Y., et al., *Accelerated Ageing Tests for Evaluations of a Durability Performance of Glass-fiber Reinforcement Polyester Composites.* Journal of Materials Science and Technology, 2010. **26**(6): p. 572-576.

[31] Marouani, S., L. Curtil, and P. Hamelin, *Ageing of carbon/epoxy and carbon/vinylester composites used in the reinforcement and/or the repair of civil engineering structures.* Composites Part B: Engineering, 2012. **43**(4): p. 2020-2030.

[32] Tsotsis, T.K., *Long-term thermo-oxidative aging in composite materials: Experimental methods.* Journal of Composite Materials, 1998. **32**(11): p. 1115-1135.

[33] Tsotsis, T.K., et al., *Aging of polymeric composite specimens for 5000 hours at elevated pressure and temperature.* Composites Science and Technology, 2001. **61**(1): p. 75-86.

[34] Tucker, R., P. Compston, and P.Y.B. Jar, *The effect of post-cure duration on the mode I interlaminar fracture toughness of glass-fibre reinforced vinylester.* Composites Part A: Applied Science and Manufacturing, 2001. **32**(1): p. 129-134.

[35] Tsotsis, T.K. and S.M. Lee, *Long-term thermo-oxidative aging in composite materials: failure mechanisms.* Composites Science and Technology, 1998. **58**(3-4): p. 355-368.

[36] Lévêque, D., et al. *Durability evaluation of carbon/BMI composites after thermal aging*. in *ICCM18: The 18th international conference on composite materials*. 2011. Jeju Korea.

[37] Colin, X., et al., *Interaction between Cracking and Oxidation in Organic Matrix Composites.* Journal of Composite Materials, 2005. **39**(15): p. 1371-1389.

[38] Abdeljaoued K., B.V., Desarmot G., Favre J. & Verdu J. *Etude de l'oxydation thermique de la matrice PMR-15*. in *11th French National Colloquium on Composite Materials : JNC 11*. 18 - 20 November 1998. Arcachon, France.

[39] Audouin, L., et al., *Role of oxygen diffusion in polymer ageing: kinetic and mechanical aspects.* Journal of Materials Science, 1994. **29**(3): p. 569-583.

[40] Buch, X. and M.E.R. Shanahan, *Thermal and thermo-oxidative ageing of an epoxy adhesive.* Polymer Degradation and Stability, 2000. **68**(3): p. 403-411.

[41] Marais C, C.X., Favre JP, Levadoux H. *Relation enter perte de masse d'un composite et thermo-oxydation de la resine : approches localer et globale*. in *11th French National Colloquium on Composite Materials : JNC 11*. 18 - 20 November 1998. Arcachon, France.

[42] Decelle, J., N. Huet, and V. Bellenger, *Oxidation induced shrinkage for thermally aged epoxy networks.* Polymer Degradation and Stability, 2003. **81**(2): p. 239-248.

[43] Tiganis, B.E., et al., *Thermal degradation of acrylonitrile–butadiene–styrene (ABS) blends.* Polymer Degradation and Stability, 2002. **76**(3): p. 425-434.

[44] Tsotsis, T., *5 - Thermo-oxidative ageing of composite materials*, in *Ageing of Composites*, R. Martin, Editor. 2008, Woodhead Publishing. p. 135.

[45] Cinquin, J. and B. Medda, *Influence of laminate thickness on composite durability for long term utilisation at intermediate temperature (100–150 °C).* Composites Science and Technology, 2009. **69**(9): p. 1432-1436.

[46] McManus, H.L., *Stress and damage in polymer matrix composite materials due to material degradation at high temperatures*. Vol. 4682.

[47] Staab, G.H., *1 - Introduction to Composite Materials*, in *Laminar Composites*, G.H. Staab, Editor. 1999, Butterworth-Heinemann: Woburn. p. 1-16.

[48] Wang, R.-M., S.-R. Zheng, and Y.-P. Zheng, *1 - Introduction to polymer matrix composites*, in *Polymer Matrix Composites and Technology*, R.-M. Wang, S.-R. Zheng, and Y.-P. Zheng, Editors. 2011, Woodhead Publishing. p. 1-548.

[49] Mallick, P.K., *Fiber-reinforced composites: materials, manufacturing, and design*. 2007: CRC press.

[50] Haque, M.H., *Thermal oxidation induced degradation of carbon fiber reinforced composites and carbon nanotube sheet enhanced fiber/matrix interface for high temperature aerospace structural applications*, in *Materials Science and Engineering*. 2012, The University of Texas at Dallas: Ann Arbor.

[51] Thevenin, R. *The composites at airbus - A long story of innovation and experience*. 2012; Available from: http://www.jeccomposites.com/webinars/composites-airbus-long-story-innovation-and-experience.

[52] Rajic, N., *13 - Non-destructive evaluation (NDE) of aerospace composites: flaw characterisation*, in *Non-Destructive Evaluation (NDE) of Polymer Matrix Composites*, V.M. Karbhari, Editor. 2013, Woodhead Publishing. p. 335-366.

[53] Dawson, D. *Composite spoilers brake Airbus for landing : CompositesWorld*. 2015; Available from: http://www.compositesworld.com/articles/composite-spoilers-brake-airbus-for-landing.

[54] X. Q. Cheng, Y.B., Z. N. Li,, *Effects of Stitching Parameters on Tensile Strength of FRPs under Hygrothermal Conditions.* Advanced Materials Research, Sep. 2012. **570**: p. 63-77.

[55] Wu, H.F., D.W. Dwight, and N.T. Huff, *Effects of silane coupling agents on the interphase and performance of glass-fiber-reinforced polymer composites.* Composites Science and Technology, 1997. **57**(8): p. 975-983.

[56] Pape, P.G., *29 - Adhesion Promoters: Silane Coupling Agents*, in *Applied Plastics Engineering Handbook*, M. Kutz, Editor. 2011, William Andrew Publishing: Oxford. p. 503-517.

[57] Margolis, J.M.E., *Properties and Performance Requirements in Advanced Thermoset Composites Industrial and Commercial Applications*. First ed. 1986, New York: Van Nostrand Reinhold Company. 282.

[58] Mensitieri, G. and M. Iannone, *9 - Modelling accelerated ageing in polymer composites*, in *Ageing of Composites*, R. Martin, Editor. 2008, Woodhead Publishing. p. 224-281.

[59] McKague, L., *ASM Handbook, Composites*. Vol. 21. 2001: ASM International.

[60] Ziel, R. *schematische Anordnung der Polymerketten in amorphen und kristallinen Bereichen*. 2009; Available from: https://commons.wikimedia.org/wiki/File:Polymerketten_-_amorph_und_kristallin.svg.

[61] Legras, H.-H.K.a.R., *Advanced Thermoplastic Composites Characterization and Processing*. 1993: Hanser Publishers.

[62] Young, R.J., *Fundamental principles of polymeric materials. 2nd edition, Stephen L. Rosen. John Wiley & Sons, New York, 1993. pp. xvi + 420, price US$68.95. ISBN 0-471-57525-9.* Polymer International, 1994. **33**(3): p. 343-344.

[63] Dieter, G., *Engineering Design A materials and Processing Approach McGraw-Hill*. New York, NY, 1991.

[64] Balasubramanian, M., *Composite Materials and Processing*. 2013: CRC Press.

[65] N/A, *MIL-HDBK-17-3F: Composite Materials Handbook, Polymer Matrix Composites: Materials Usage, Design, and Analysis*. Vol. 3. 2002: US Department of Defense.

[66] Darvell, B.W., *Chapter 3 - Polymers*, in *Materials Science for Dentistry (Ninth edition)*, B.W. Darvell, Editor. 2009, Woodhead Publishing. p. 60-81.

[67] Lincoln, B., Kenneth J. Gomes, and James F. Braden, *Mechanical Fastening of Plastics: An Engineering Handbook*. Vol. Chapter 1. 1984, New York: M. Dekker.

[68] Prime, R.B., *"Thermosets" in Thermal Characterization of Polymeric Materials. Chapter 6*. 1997, San Diego: Academic Press.

[69] Kumar, R., T. Singh, and H. Singh, *Natural Fibers Polymeric Composites with Particulate Fillers–A review report.* International Journal of Advanced Engineering Research and Applications (IJAERA), 2015. **1**(1).

[70] Dostal, C.A., Woods, M. S. and Ronke, A. W. (Eds.), *Engineered Materials Handbook*. Vol. 1. 1987, Metals Park, Ohio: ASM Internation.

[71] Hull, D. and T.W. Clyne., *An Introduction to Composite Materials*. 1996: Cambridge University Press.

[72] Ellis, B., *Introduction to the chemistry, synthesis, manufacture and characterization of epoxy resins*, in *Chemistry and Technology of Epoxy Resins*, B. Ellis, Editor. 1993, Springer Netherlands. p. 1-36.

[73] Bauer, R.S. *Application of Epoxy Resins in Advanced Composites*. in *Proc. 34th Internatl.SAMPE Symposium*. May 8-11,1989. Reno, Nevada.

[74] T. Alfrey, J., *Applied Polymer Science*. Vol. Chapter 11. 1985, Washington D.C.: American Chemical Society.

[75] Mathot, V.B.F., *Calorimetry and Thermal Analysis of Polymers*. 1994, Munich: Hanser.

[76] A.D Jenkins, P.K., R.F.T. Stepto and U.W. Suter, *Glossary of Basic Terms in Polymer Science.* Pure and Applied Chemistry, 1996. **68**: p. 2287.

[77] K. Hatada, R.B.F., J. Kahovec, E. Maréchal, I. Mita and V. Shibaev, *Definitions of terms relating to degradation, aging, and related chemical transformations of polymers.* Pure and Applied Chemistry, 1996. **68**: p. 2313.

[78] Roller, M.B., *Thermoset and coatings technology: The challenge of interdisciplinary chemistry.* Polymer Engineering & Science, 1979. **19**(10): p. 692-698.

[79] Whitesell, M.A.F.a.J.K., *Organic Chemistry*. 1994, Jones and Bartlett Publishers: Boston.

[80] Bauer, R. *Application of epoxy resins in advanced composites*. in *34th Internatl. SAMPE Symposium*. 1989. Reno, Nevada.

[81] O'Neill, L.A. and C.P. Cole, *Chemical and spectroscopic studies of epoxy resin reactions in the surface coating field.* Journal of Applied Chemistry, 1956. **6**(8): p. 356-364.

[82] Li, M., *Temperature and moisture effects on composite materials for wind turbine blades*, in *Chemical Engineering*. March 2000, Montana State University-Bozeman: Bozeman, Montana.

[83] *Department of defense handbook aircraft structural integrity program (MIL-HDBK-1530A(USAF))*. 2002, USA: Department of Defense of the United Stated of America.

[84] J.B. Ransom, E.H.G., I.S. Raju, N.F. Knight, Jr. , and J.R. Reeder, *Lessons Learned from Recent Failure and Incident Investigations of Composite Structures*, in *49th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference*. Apr 07, 2008, NASA NTRS: Schaumburg, IL; United States.

[85] Hodge, I.M., *Physical Aging in Polymer Glasses.* Science, 1995. **267**(5206): p. 1945-1947.

[86] Odegard, G.M. and A. Bandyopadhyay, *Physical aging of epoxy polymers and their composites.* Journal of Polymer Science, Part B: Polymer Physics, 2011. **49**(24): p. 1695-1716.

[87] Lin, Y.G., H. Sautereau, and J.P. Pascault, *Epoxy network structure effect on physical aging behavior.* Journal of Applied Polymer Science, 1986. **32**(4): p. 4595-4605.

[88] Kong, E.-W., *Physical aging in epoxy matrices and composites*, in *Epoxy Resins and Composites IV*, K. Dušek, Editor. 1986, Springer Berlin Heidelberg. p. 125-171.

[89] Oyanguren, P.A., et al., *Rejuvenation of epoxy glasses subjected to uniaxial compression.* Polymer, 1994. **35**(24): p. 5279-5282.

[90] Kong, E.S.-W., et al., *Physical aging of linear and network epoxy resins.* Polymer Engineering & Science, 1981. **21**(14): p. 943-950.

[91] Chang, T.D. and J.O. Brittain, *Studies of epoxy resin systems: Part C: Effect of sub-Tg aging on the physical properties of a fully cured epoxy resin.* Polymer Engineering & Science, 1982. **22**(18): p. 1221-1227.

[92] Hu, H.W., *Physical Aging in Long Term Creep of Polymeric Composite Laminates.* Journal of Mechanics, 2007. **23**(03): p. 245-252.

[93] Lévêque, D., et al., *Analysis of how thermal aging affects the long-term mechanical behavior and strength of polymer–matrix composites.* Composites Science and Technology, 2005. **65**(3–4): p. 395-401.

[94] Shi, X., B.M.D. Fernando, and S. Croll, *Concurrent physical aging and degradation of crosslinked coating systems in accelerated weathering.* Journal of Coatings Technology and Research, 2008. **5**(3): p. 299-309.

[95] Cook, W.D., M. Mehrabi, and G.H. Edward, *Ageing and yielding in model epoxy thermosets.* Polymer, 1999. **40**(5): p. 1209-1218.

[96] G.'Sell, C. and G.B. McKenna, *Influence of physical ageing on the yield response of model DGEBA/poly(propylene oxide) epoxy glasses.* Polymer, 1992. **33**(10): p. 2103-2113.

[97] Chang, T.D. and J.O. Brittain, *Studies of epoxy resin systems: Part D: Fracture toughness of an epoxy resin: A study of the effect of crosslinking and sub-Tg aging.* Polymer Engineering & Science, 1982. **22**(18): p. 1228-1236.

[98] Truong, V.T. and B.C. Ennis, *Effect of physical aging on the fracture behavior of crosslinked epoxies.* Polymer Engineering & Science, 1991. **31**(8): p. 548-557.

[99] Barral, L., et al., *Physical aging of an epoxy/cycloaliphatic amine resin.* European Polymer Journal, 1999. **35**(3): p. 403-411.

[100] Barral, L., et al., *Physical aging of a tetrafunctional/phenol novolac epoxy mixture cured with diamine DSC and DMA measurements.* Journal of Thermal Analysis and Calorimetry, 2000. **60**(2): p. 391-399.

[101] Montserrat, S., *Physical aging studies in epoxy resins. I. Kinetics of the enthalpy relaxation process in a fully cured epoxy resin.* Journal of Polymer Science Part B: Polymer Physics, 1994. **32**(3): p. 509-522.

[102] Fraga, F., et al., *Physical aging for an epoxy network diglycidyl ether of bisphenol A/m-xylylenediamine.* Polymer, 2003. **44**(19): p. 5779-5784.

[103] Fraga, F., et al., *Comparative study of the physical aging of the epoxy systems BADGE n = 0/m-XDA and BADGE n = 0/m-XDA/PEI.* Journal of Applied Polymer Science, 2007. **103**(6): p. 3931-3935.

[104] Montserrat, S., et al., *Effect of crosslink length on the enthalpy relaxation of fully cured epoxy–diamine resins.* Journal of Polymer Science Part B: Polymer Physics, 2000. **38**(3): p. 456-468.

[105] Montserrat, S., Y. Calventus, and J.M. Hutchinson, *Physical aging of thermosetting powder coatings.* Progress in Organic Coatings, 2006. **55**(1): p. 35-42.

[106] Ramírez, C., et al., *Study of the physical aging of an epoxy/cycloaliphatic amine resin modified with abs.* Journal of Thermal Analysis and Calorimetry, 2002. **70**(1): p. 85-92.

[107] Ramírez, C., et al., *Enthalpy relaxation in an epoxy-cycloaliphatic amine resin.* Colloid and Polymer Science, 2001. **279**(2): p. 184-189.

[108] Hutchinson, J.M., et al., *Enthalpy relaxation in a partially cured epoxy resin.* Journal of Polymer Science Part B: Polymer Physics, 1996. **34**(2): p. 229-239.

[109] Plazek, D.J. and Z.N. Frund, *Epoxy resins (DGEBA): The curing and physical aging process.* Journal of Polymer Science Part B: Polymer Physics, 1990. **28**(4): p. 431-448.

[110] Ophir, Z.H., J.A. Emerson, and G.L. Wilkes, *Sub-Tg annealing studies of rubber-modified and unmodified epoxy systems.* Journal of Applied Physics, 1978. **49**(10): p. 5032-5038.

[111] Kawakami, H. and M. Watanabe, *Changes in the thermomechanical behavior of epoxy glasses under the state of strain aging.* Journal of Applied Polymer Science, 2008. **107**(4): p. 2095-2100.

[112] Zheng, Y. and G.B. McKenna, *Structural Recovery in a Model Epoxy: Comparison of Responses after Temperature and Relative Humidity Jumps.* Macromolecules, 2003. **36**(7): p. 2387-2396.

[113] Wang, B., et al., *Influence of physical aging and side group on the free volume of epoxy resins probed by positron.* Polymer, 2003. **44**(14): p. 4047-4052.

[114] Fraga, F., et al., *Kinetics of the enthalpy relaxation process for an epoxy network as determined with a peak shift model.* Journal of Applied Polymer Science, 2005. **98**(5): p. 2003-2008.

[115] Leon Yu, T. and Y.S. Chen, *Physical aging of epoxy resin blended with poly(ether sulfone): Effect of poly(ether sulfone) molecular weight.* Journal of Polymer Research, 2000. **7**(4): p. 257-266.

[116] Fraga, F., et al., *Kinetic analysis of relaxation process for the epoxy network diglycidyl ether of bisphenol A/m-xylylenediamine.* Journal of Applied Polymer Science, 2005. **96**(5): p. 1591-1595.

[117] Stocchi, A., et al., *Physical and water aging of glass fiber-reinforced plastic pipes.* Composite Interfaces, 2006. **13**(8-9): p. 685-697.

[118] Lu, H. and S. Nutt, *Restricted Relaxation in Polymer Nanocomposites near the Glass Transition.* Macromolecules, 2003. **36**(11): p. 4010-4016.

[119] Jong, S.R. and T.L. Yu, *Physical aging of epoxy resin blended with a medium molecular weight poly(ether sulfone).* Macromolecular Chemistry and Physics, 1999. **200**(1): p. 87-94.

[120] Jong, S.R. and T.L. Yu, *Physical aging of poly(ether sulfone)-modified epoxy resin.* Journal of Polymer Science Part B: Polymer Physics, 1997. **35**(1): p. 69-83.

[121] Morancho, J.M. and J.M. Salla, *Relaxation in partially cured samples of an epoxy resin and of the same resin modified with a carboxyl-terminated rubber.* Polymer, 1999. **40**(10): p. 2821-2828.

[122] Tarifa, S. and A. Bouazizi, *Glass transitions in crosslinked epoxy networks.* Journal of thermal analysis, 1997. **48**(2): p. 297-307.

[123] Morancho, J.M. and J.M. Salla, *Relaxation in a neat epoxy resin and in the same resin modified with a carboxyl-terminated copolymer.* Journal of Non-Crystalline Solids, 1998. **235–237**: p. 596-599.

[124] Montserrat, S., et al., *Structural relaxation in fully cured epoxy resins.* Journal of Non-Crystalline Solids, 1994. **172–174, Part 2**: p. 1017-1022.

[125] Cortés, P., S. Montserrat, and J.M. Hutchinson, *Addition of a reactive diluent to a catalyzed epoxy-anhydride system. II. effect on enthalpy relaxation.* Journal of Applied Polymer Science, 1997. **63**(1): p. 17-25.

[126] Breach, C.D., M.J. Folkes, and J.M. Barton, *Physical ageing of an epoxy resin/polyethersulphone blend.* Polymer, 1992. **33**(14): p. 3080-3082.

[127] Fraga, F., et al., *Study of the Physical Aging of the Epoxy System BADGE n=0/m-XDA/CaCO3.* Journal of Applied Polymer Science, 2009. **113**(4): p. 2456-2461.

[128] Issoupov, V., et al., *Thermally stimulated creep (TSCr) study of viscoelastic behavior and physical aging of a polymeric matrix composite for spacecraft structures.* Journal of Applied Polymer Science, 2002. **85**(2): p. 342-350.

[129] Mendelsy, D.-A., et al., *The Influence of Internal Stresses on the Microbond Test II: Physical Aging and Adhesion.* Journal of Composite Materials, 2002. **36**(14): p. 1655-1676.

[130] Brinson, L.C. and T.S. Gates, *2.10 - Viscoelasticity and Aging of Polymer Matrix Composites*, in *Comprehensive Composite Materials*, A.K. Zweben, Editor. 2000, Pergamon: Oxford. p. 333-368.

[131] Hiltz, J.A., *Low Temperature Thermal Degradation Studies of Styrene Cross-Linked Vinyl Ester and Polyester Resins*. 1988: Defence Research Establishment Atlantic.

[132] Trabelsi, W., *Ageing of a carbon/epoxy composite for aeronautic applications*. 2006, Arts et Métiers ParisTech.

[133] Ghosh, S., et al., *Thermal degradation and ageing of segmented polyamides.* Polymer Degradation and Stability, 2000. **67**(3): p. 427-436.

[134] Pielichowski, K., J. Njuguna, and R.T. Limited, *Thermal Degradation of Polymeric Materials*. 2005: Rapra Technology.

[135] Ebewele, R.O., *Polymer Science and Technology*. 2000: CRC Press.

[136] Maxwell, A.S., Broughton, W R, Dean, G D, Sims, G D, *Review of accelerated ageing methods and lifetime prediction techniques for polymeric materials.* NPL Report DEPC-MPR 016, March 2005, 2005.

[137] Wright, D.C. and R.T. Limited, *Failure of Plastics and Rubber Products: Causes, Effects, and Case Studies Involving Degradation*. Vol. Chapter 2. 2001: Rapra Technology.

[138] Voigt, J., *Atmospheric Oxidation and Antioxidants. Von G. Scott. Elsevier Publishing Company, Amsterdam-London-New York 1965. X, 528 S., zahlr. Abb., geb. Dfl. 72.50.* Angewandte Chemie, 1966. **78**(22): p. 1027-1027.

[139] Zweifel, H., *Principles of Oxidative Degradation*, in *Stabilization of Polymeric Materials*. 1998, Springer Berlin Heidelberg. p. 1-40.

[140] Lv, X., et al., *Effect of thermal-oxidative aging on carbon fibre-bismaleimide composites.* Pigment and Resin Technology, 2012. **41**(1): p. 34-41.

[141] Abrate, S., *Impact on Laminated Composites: Recent Advances.* Applied Mechanics Reviews, 1994. **47**(11): p. 517-544.

[142] Carbas, R.J.C., et al., *Effect of post-cure on the glass transition temperature and mechanical properties of epoxy adhesives.* Journal of Adhesion Science and Technology, 2013. **27**(23): p. 2542-2557.

[143] Bockenheimer, C., D. Fata, and W. Possart, *New aspects of aging in epoxy networks. I. Thermal aging.* Journal of Applied Polymer Science, 2004. **91**(1): p. 361-368.

[144] Cherdoud-Chihani, A., M. Mouzali, and M.J.M. Abadie, *Study of crosslinking AMS/DGEBA system by FTIR.* Journal of Applied Polymer Science, 1998. **69**(6): p. 1167-1178.

[145] Galant, C., et al., *Thermal and radio-oxidation of epoxy coatings.* Progress in Organic Coatings, 2010. **69**(4): p. 322-329.

[146] Pei, Y.M., et al., *Thermal-oxidative aging of DGEBA/EPN/LMPA epoxy system: Chemical structure and thermal-mechanical properties.* Polymer Degradation and Stability, 2011. **96**(7): p. 1179-1186.

[147] Zahra, Y., et al., *Thermo-oxidative aging of epoxy coating systems.* Progress in Organic Coatings, 2014. **77**(2): p. 380-387.

[148] Parvatareddy, H., et al., *Environmental aging of high-performance polymeric composites: Effects on durability.* Composites Science and Technology, 1995. **53**(4): p. 399-409.

[149] Xiao, H.M., et al., *Microstructure evolution of SW/EPN composites during hot air aging.* Journal of Applied Polymer Science, 2014. **131**(8).

[150] Colin, X. and J. Verdu, *Strategy for studying thermal oxidation of organic matrix composites.* Composites Science and Technology, 2005. **65**(3-4): p. 411-419.

[151] Ozcelik, O., L. Aktas, and M.C. Altan, *Thermo-oxidative degradation of graphite/epoxy composite laminates: Modeling and long-term predictions.* Express Polymer Letters, 2009. **3**(12): p. 797-803.

[152] Liu, Y.L., et al., *Novel thermosetting resins based on 4-(N-maleimido)phenylglycidylether: III. Studies on the thermal degradation kinetics and mechanisms of the cured resins.* Polymer Degradation and Stability, 2004. **86**(1): p. 135-145.

[153] Mailhot, B., et al., *Study of the degradation of an epoxy/amine resin, 1 photo- and thermo-chemical mechanisms.* Macromolecular Chemistry and Physics, 2005. **206**(5): p. 575-584.

[154] Wolfrum, J., S. Eibl, and L. Lietch, *Rapid evaluation of long-term thermal degradation of carbon fibre epoxy composites.* Composites Science and Technology, 2009. **69**(3-4): p. 523-530.

[155] Awaja, F. and P.J. Pigram, *Surface molecular characterisation of different epoxy resin composites subjected to UV accelerated degradation using XPS and ToF-SIMS.* Polymer Degradation and Stability, 2009. **94**(4): p. 651-658.

[156] Dyakonov, T., et al., *Thermal analysis of some aromatic amine cured model epoxy resin systems - II: Residues of degradation.* Polymer Degradation and Stability, 1996. **54**(1): p. 67-83.

[157] Levchik, S.V., et al., *Epoxy resins cured with aminophenylmethylphosphine oxide—II. Mechanism of thermal decomposition.* Polymer Degradation and Stability, 1998. **60**(1): p. 169-183.

[158] Grassie, N., M.I. Guy, and N.H. Tennent, *Degradation of epoxy polymers: Part 4-Thermal degradation of bisphenol-A diglycidyl ether cured with ethylene diamine.* Polymer Degradation and Stability, 1986. **14**(2): p. 125-137.

[159] Liu, Y.L., et al., *Phosphorus-containing epoxy for flame retardance: IV. Kinetics and mechanism of thermal degradation.* Polymer Degradation and Stability, 1997. **56**(3): p. 291-299.

[160] Rose, N., et al., *Thermal oxidative degradation of an epoxy resin.* Polymer Degradation and Stability, 1993. **42**(3): p. 307-316.

[161] Lin, S.C.B., B. J. Pearce, E. M., *Epoxy resins-3. Application of fourier transform IR to degradation studies of epoxy systems.* Journal of polymer science. Part A-1, Polymer chemistry, 1979. **17**(10): p. 3121-3148.

[162] Musto, P., et al., *Thermal-oxidative degradation of epoxy and epoxy-bismaleimide networks: Kinetics and mechanism.* Macromolecular Chemistry and Physics, 2001. **202**(18): p. 3445-3458.

[163] Li, K., et al., *The change of thermal-mechanical properties and chemical structure of ambient cured DGEBA/TEPA under accelerated thermo-oxidative aging.* Polymer Degradation and Stability, 2013. **98**(11): p. 2340-2346.

[164] Akay, M. and G.R. Spratt, *Evaluation of thermal ageing of a carbon fibre reinforced bismalemide.* Composites Science and Technology, 2008. **68**(15–16): p. 3081-3086.

[165] Kumar, B.G., R.P. Singh, and T. Nakamura, *Degradation of Carbon Fiber-Reinforced Epoxy Composites by Ultraviolet Radiation and Condensation.* Journal of Composite Materials, 2002. **36**(24): p. 2713-2733.

[166] Rmili, W., et al., *Dynamic Mechanical Properties and Thermal Effect of an Epoxy Resin Composite, Encapsulation's Element of a New Electronic Component.* Journal of Electronic Materials, 2014. **43**(3): p. 702-707.

[167] Kerber, R., *W. Schnabel: Polymer Degradation, Principles and Practical Applications. Carl Hanser Verlag, München 1981. 227 Seiten, Preis: DM 68,—.* Berichte der Bunsengesellschaft für physikalische Chemie, 1983. **87**(9): p. 838-839.

[168] Emanuel', N.N.M. and A.L. Buchachenko, *Chemical Physics of Polymer Degradation And Stabilization*. 1987, Utrecht, Netherlands VNU Science Press.

[169] Luoma, G.A. and R.D. Rowland, *Environmental degradation of an epoxy resin matrix.* Journal of Applied Polymer Science, 1986. **32**(7): p. 5777-5790.

[170] Hong, S.G., *The thermal-oxidative degradation of an epoxy adhesive on metal substrates: XPS and RAIR analyses.* Polymer Degradation and Stability, 1995. **48**(2): p. 211-218.

[171] Damian, C., E. Espuche, and M. Escoubes, *Influence of three ageing types (thermal oxidation, radiochemical and hydrolytic ageing) on the structure and gas transport properties of epoxy–amine networks.* Polymer Degradation and Stability, 2001. **72**(3): p. 447-458.

[172] Bellenger, V. and J. Verdu, *Oxidative skeleton breaking in epoxy–amine networks.* Journal of Applied Polymer Science, 1985. **30**(1): p. 363-374.

[173] Griffiths, R.P., *Physical ageing effects in crosslinked epoxy resins*. 1988, University of Brunel: University of Brunel

[174] MacKenzie, S.J., *Material properties of bi-modal epoxy networks*. ARL/TR (Aberdeen Proving Ground, Md.) ;, ed. T.J. Mulkern, N.C. Beck Tan, and U.S.A.R. Laboratory. 2001, Aberdeen Proving Ground, MD: Army Research Laboratory.

[175] Costa, M.L., et al., *Avaliação térmica e reológica do ciclo de cura do pré-mpregnado de carbono/epóxi*. Polímeros: Ciência e Tecnologia, 2003. **13**(3): p. 188-197.

[176] Wingard, C.D., *Characterization of prepreg and cured epoxy/fiberglass composite material for use in advanced composite piping systems.* Thermochimica Acta, 2000. **357-358**: p. 293-301.

[177] Hayes, B.S., E.N. Gilbert, and J.C. Seferis, *Scaling complications of dual temperature cure resin prepreg systems in airplane part manufacture.* Composites Part A: Applied Science and Manufacturing, 2000. **31**(7): p. 717-725.

[178] Shim, S.B., et al., *Thermal characterization and comparison of structural prepregs with different cure temperatures.* Thermochimica Acta, 1997. **291**(1-2): p. 73-79.

[179] S. Pangrle, C.S.W.a.P.H.G., *Low temperature relaxation of DGEBA epoxy resins: A thermally stimulated discharge current (TSDC) study.* Polymer Composites, 1989. **10**: p. 173.

[180] Pederson, C.L., et al., *The effect of isothermal aging on transverse crack development in carbon fiber reinforced cross-ply laminates.* Polymer Composites, 1995. **16**(2): p. 154-160.

[181] Bullions, T.A., J.E. McGrath, and A.C. Loos, *Thermal-oxidative aging effects on the properties of a carbon fiber-reinforced phenylethynyl-terminated poly(etherimide).* Composites Science and Technology, 2003. **63**(12): p. 1737-1748.

[182] Dao, B., et al., *Accelerated aging versus realistic aging in aerospace composite materials. II. Chemistry of thermal aging in a structural composite*. Journal of Applied Polymer Science, 2006. **102**(4): p. 3221-3232.

[183] Dao, B., et al., *Accelerated ageing versus realistic ageing in aerospace composite materials. III. the chemistry of thermal ageing in bismaleimide based composites.* Journal of Applied Polymer Science, 2007. **105**(4): p. 2062-2072.

[184] Ammar-Khodja, I., et al., *Preliminary results on thermo-oxidative ageing of multi-hole carbon/epoxy composites.* Composites Science and Technology, 2009. **69**(9): p. 1427-1431.

[185] Tian, W. and J. Hodgkin, *Long-term aging in a commercial aerospace composite sample: Chemical and physical changes.* Journal of Applied Polymer Science, 2010. **115**(5): p. 2981-2985.

[186] Colin X., M.C.C.J. *Kinetic modelling of weight changes during the isothermal oxidative ageing of bismaleimide matrix*. in *DURACOSYS 99*. 1999. Brussels.

[187] Teston, B., et al. *Comportement thermique d'un adhésif bismaléimide modifié époxyde*. in *JNC*. 2000. Cachan.

[188] Colin, X., C. Marais, and J. Verdu, *A new method for predicting the thermal oxidation of thermoset matrices: Application to an amine crosslinked epoxy.* Polymer Testing, 2001. **20**(7): p. 795-803.

[189] Tsotsis, T.K., et al., *Preliminary evaluation of the use of elevated pressure to accelerate thermo-oxidative aging in composites.* Polymer Degradation and Stability, 1999. **64**(2): p. 207-212.

[190] Kobayashi, Y. and S. Kobayashi, *The effect of long-term exposure to high temperature atmosphere on weight change and damage progress in carbon fiber-reinforced polycyanate ester composites.* Advanced Composite Materials, 2015. **24**(2): p. 97-112.

[191] Colin, X., C. Marais, and J. Verdu, *Kinetic modelling and simulation of gravimetric curves: application to the oxidation of bismaleimide and epoxy resins.* Polymer Degradation and Stability, 2002. **78**(3): p. 545-553.

[192] Tsotsis, T.K., et al., *3000 hours aging of polymeric composite specimens under elevated pressure and temperature.* 44th International SAMPE Symposium, 1999.

[193] Tsotsis, T.K., *Thermo-oxidative aging of composite materials.* Journal of Composite Materials, 1995. **29**(3): p. 410-422.

[194] Woelke, P., N. Abboud, and I. Sandler. *Framework for constitutive modeling and life prediction for polymeric matrix composites*. in *Society for Experimental Mechanics - SEM Annual Conference and Exposition on Experimental and Applied Mechanics 2009*. 2009.

[195] Madhukar, M.S., K.J. Bowles, and D.S. Papadopoulos, *Thermo-Oxidative Stability and Fiber Surface Modification Effects on the Inplane Shear Properties of Graphite/PMR-15 Composites.* Journal of Composite Materials, 1997. **31**(6): p. 596-618.

[196] Tijssens, M.G.A., E.v.d. Giessen, and L.J. Sluys, *Simulation of mode I crack growth in polymers by crazing.* International Journal of Solids and Structures, 2000. **37**(48–50): p. 7307-7327.

[197] Vu, D.Q., M. Gigliotti, and M.C. Lafarie-Frenot, *Experimental characterization of thermo-oxidation-induced shrinkage and damage in polymer-matrix composites.* Composites Part A: Applied Science and Manufacturing, 2012. **43**(4): p. 577-586.

[198] Lafarie-Frenot, M.C. and S. Rouquie, *Influence of oxidative environments on damage in c/epoxy laminates subjected to thermal cycling.* Composites Science and Technology, 2004. **64**(10-11): p. 1725-1735.

[199] Bowles KJ, P.D., Inghram L, McCorkle L, Klan OV, *Longtime durability of PMR15 matrix polymer at 204, 260, 288, and 316 °C.* NASA/TM-2001-210602; 2001., 2001.

[200] Vu, D.-Q., M. Gigliotti, and M.C. Lafarie-Frenot, *The effect of thermo-oxidation on matrix cracking of cross-ply [0/90]S composite laminates.* Composites Part A: Applied Science and Manufacturing, 2013. **44**(0): p. 114-121.

[201] McMahon, P.E., *Thermal oxidative resistance of carbon fibres and their composites.* 23rd national SAMPE symposium proceedings 1978. **1978;23:150**.

[202] Bowles, K.J., et al., *The effects of fiber surface modification and thermal aging on composite toughness and its measurement.* Journal of Composite Materials, 1997. **31**(6): p. 552-579.

[203] Jangchud, I., et al., *Studies of PAN-based carbon fiber surfaces: Their influence on interfacial bonding with PMR-15 polyimide and composite thermo-oxidative stability.* Journal of Advanced Materials, 1996. **28**(1): p. 19-25.

[204] Scola, D.A., B.L. Laube, and J.H. Vontell, *Interface characteristics of isothermally aged high temperature graphite fiber/PMR-15 composites.* Proc. of the 3rd Int. Conf. on Comp. Interfaces (ICCI-III), 1990: p. 17-36.

[205] Kausch, H.H. and C. Oudet, *Progress and challenge in polymer crazing and fatigue.* Makromolekulare Chemie. Macromolecular Symposia, 1988. **22**(1): p. 207-224.

[206] Gigliotti, M., et al., *Local shrinkage and stress induced by thermo-oxidation in composite materials at high temperatures.* Journal of the Mechanics and Physics of Solids, 2011. **59**(3): p. 696-712.

[207] Wells, J.K. and P.W.R. Beaumont, *Debonding and pull-out processes in fibrous composites.* Journal of Materials Science, 1985. **20**(4): p. 1275-1284.

[208] Evans, A.G. and F.W. Zok, *The physics and mechanics of fibre-reinforced brittle matrix composites.* Journal of Materials Science, 1994. **29**(15): p. 3857-3896.

[209] Zafeiropoulos, N.E., C.A. Baillie, and J.M. Hodgkinson, *Engineering and characterisation of the interface in flax fibre/polypropylene composite materials. Part II. The effect of surface treatments on the interface.* Composites Part A: Applied Science and Manufacturing, 2002. **33**(9): p. 1185-1190.

[210] Dlouhy, I., et al., *Fracture behaviour of hybrid glass matrix composites: thermal ageing effects.* Composites Part A: Applied Science and Manufacturing, 2003. **34**(12): p. 1177-1185.

[211] *ASTM D5229 / D5229M - 14 Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials*. 2014, ASTM International: West Conshohocken, PA.

[212] *EHG250-68-37.pdf*. 2015; Available from: https://www.yumpu.com/en/document/view/9044772/ehg250-68-37-prepreg-materials-for-secondary-structures-gurit.

[213] *ASTM D5229 / D5229M - 14 Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials.* 2015.

[214] *ASTM D3039 / D3039M - 14 Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials.* 2015.

[215] *ASTM D7028 - 07e1 Standard Test Method for Glass Transition Temperature (DMA Tg) of Polymer Matrix Composites by Dynamic Mechanical Analysis (DMA).* 2015.

[216] Lofthouse, M.G. and P. Burroughs, *Materials testing by Dynamic mechanical analysis.* Journal of thermal analysis, 1978. **13**(3): p. 439-453.

[217] O'Neal, H., et al., *Comparison of Tg values for a graphite epoxy composite by differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA).* Journal of advanced materials, 1995. **26**(3): p. 49-54.

[218] Yousefi, A., P.G. Lafleur, and R. Gauvin, *Kinetic studies of thermoset cure reactions: A review.* Polymer Composites, 1997. **18**(2): p. 157-168.

[219] Lee, C.Y.C. and I.J. Goldfarb, *Glass transition temperature (Tg) determination of partially cured thermosetting systems.* Polymer Engineering & Science, 1981. **21**(12): p. 787-791.

[220] Follensbee, R.A., et al., *Development of dynamic mechanical methods to characterize the cure state of phenolic resole resins.* Journal of Applied Polymer Science, 1993. **47**(8): p. 1481-1496.

[221] Vaidyanathan, J. and T.K. Vaidyanathan, *Dynamic mechanical analysis of heat, microwave and visible light cure denture base resins.* Journal of Materials Science: Materials in Medicine, 1995. **6**(11): p. 670-674.

[222] Schneider, N.S. and J.K. Gillham, *TBA studies of prepreg curing behavior.* Polymer Composites, 1980. **1**(2): p. 97-102.

[223] Kosfeld, R., et al., *The influence of interphases on properties of epoxy resin composites.* Makromolekulare Chemie. Macromolecular Symposia, 1993. **76**(1): p. 269-281.

[224] Ding, J., C. Chen, and G. Xue, *The dynamic mechanical analysis of epoxy–copper powder composites using azole compounds as coupling agents.* Journal of Applied Polymer Science, 1991. **42**(5): p. 1459-1464.

[225] Hurwitz, F.I., *Dynamic mechanical characterization of cure of a polyimide-graphite fiber composite (PMR 15/Celion 6000).* Polymer Composites, 1983. **4**(2): p. 90-97.

[226] Bilyeu, B., *Characterization of cure kinetics and physical properties of a high performance, glass fiber-reinforced epoxy prepreg and a novel fluorine-modified, amine-cured commercial epoxy*, in *Materials Science and Engineering*. 2003, University of North Texas. p. chapter 2.

[227] Fleszar, M.F., *Differential Scanning Calorimetry as a Quality Control Method for Epoxy Resin Prepreg*. 1988, DTIC Document.

[228] Dao, B., et al., *Accelerated ageing versus realistic ageing in aerospace composite materials. III. the chemistry of thermal ageing in bismaleimide based composites.* J Appl Poly Sci, 2007. **105**(4): p. 2062-2072.

[229] Dao, B., et al., *Accelerated aging versus realistic aging in aerospace composite materials. I. The chemistry of thermal aging in a low-temperature-cure epoxy composite.* J Appl Poly Sci, 2006. **102**(5): p. 4291-4303.

[230] Dao, B., et al., *Accelerated aging versus realistic aging in aerospace composite materials. II. Chemistry of thermal aging in a structural composite.* J Appl Poly Sci, 2006. **102**(4): p. 3221-3232.

[231] Kingery, W.D., et al., *Introduction to Ceramics.* Journal of The Electrochemical Society, 1977. **124**(3): p. 152C.

[232] Odegard, G.M. and A. Bandyopadhyay, *Physical aging of epoxy polymers and their composites.* J Poly Sci Part B Poly Phys, 2011. **49**(24): p. 1695-1716.

[233] Grassie, N., M.I. Guy, and N.H. Tennent, *Degradation of epoxy polymers: Part 4-Thermal degradation of bisphenol-A diglycidyl ether cured with ethylene diamine.* Poly Degrad Stabil, 1986. **14**(2): p. 125-137.

[234] Liu, Y.L., et al., *Phosphorus-containing epoxy for flame retardance: IV. Kinetics and mechanism of thermal degradation.* Poly Degrad Stabil, 1997. **56**(3): p. 291-299.

[235] Rose, N., et al., *Thermal oxidative degradation of an epoxy resin.* Poly Degrad Stabil, 1993. **42**(3): p. 307-316.

[236] Musto, P., et al., *Thermal-oxidative degradation of epoxy and epoxy-bismaleimide networks: Kinetics and mechanism.* Macromol Chem Phys, 2001. **202**(18): p. 3445-3458.

[237] Bondzic, S., et al., *Chemistry of thermal ageing in aerospace epoxy composites.* J Appl Poly Sci, 2006. **100**(3): p. 2210-2219.

[238] Ammar-Khodja, I., et al., *Preliminary results on thermo-oxidative ageing of multi-hole carbon/epoxy composites.* Comp Sci Technol, 2009. **69**(9): p. 1427-1431.

[239] Hinkley, J. and J. Connell, *Resin Systems and Chemistry: Degradation Mechanisms and Durability*, in *Long-Term Dura Poly Matrix Comp*, K.V. Pochiraju, G.P. Tandon, and G.A. Schoeppner, Editors. 2012, Springer US: New York, NY. p. 1-37.

[240] Rose, N., et al., *Comprehensive study of the oxidative degradation of an epoxy resin using the degradation front model.* Polymer Degradation and Stability, 1996. **54**(2–3): p. 355-360.