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PREVENTION OF ENVIRONMENTAL DEGRADATION OF EPOXY RESINS MODIFIED WITH THE ADDITION OF DIFFERENT FILLERS

Submitted by

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Abstract

Timber composites such as glulam beams are increasingly being used outdoors where their service life depends to a large extent on the durability of the adhesive used in the composite. Enhancing the durability of epoxy resins used in such composite materials would prolong their service life and enable them to compete more effectively with other structural materials such as concrete and steel. The weathering of timber composites is caused by a complex combination of chemical, thermal, physical and mechanical effects. This study sought to improve our understanding of the photodegradation of two epoxy resins and the relationship between timber and epoxy resin photodegradation. The effectiveness of the following fillers applied in two epoxy resins of protecting from photodegradation was investigated: functionalised multi-walled carbon nanotubes, microcrystalline cellulose, and calcium sulfate. First, the effect of accelerated weathering on the properties of two epoxy resins (hydrogenated diglycidyl ether of bisphenol A, HDGEBA, aliphatic epoxy) and (diglycidyl ether of bisphenol A, DGEBA, aromatic epoxy) was followed by exposing to accelerated weathering conditions, which are UV irradiation (UVA-240 nm), moisture, and increased temperature with different accelerated weathering times (1, 2, 3, 4, and 6 months). All samples after exposure were examined for structural and chemical changes of the epoxy resin specimens and were analysed using Fourier Transform Infrared (FTIR) spectroscopy, thermal tests, mechanical tests, and Scanning Electron Microscopy (SEM). The overall results obtained showed that epoxy composites exhibited ore resistant to reduce degradation when exposed to different accelerated weathering.

The initial exposure time of one and two months did not show significant changes in the chemical, thermal, and mechanical properties of epoxy resins and epoxy composites. HDGEBA incorporated CS and MWCNT showed the highest potential to improve the resistance to increase photodegradation, which was approved by the FTIR (carbonyl and hydroxy indices), thermal (TGA and DSC), mechanical (tensile strength), and morphology tests after exposure to different accelerated weathering times. The results of chemical degradation were evaluated by using carbonyl and hydroxyl index, which indicated that HDGEBA and HDGEBA composites have lower carbonyl and hydroxyl indices after exposure to accelerated weathering with different times compared to those of DGEBA and DGEBA composites. The results of mechanical tests before and upon exposure to accelerated weathering showed that DGEBA and DGEBA composites have a higher tensile strength and lower elongation at break compared to those of HDGEBA and HDGEBA composites. However, after exposure to six months accelerated weathering, the HDGEBA and HDGEBA composites exhibited more resistance to a reduction in tensile strength compared to those of DGEBA and DGEBA epoxy composites. The tensile strength of DGEBA /2% CS and DGEBA /0.5% MWCNT composites showed higher tensile strength and less elongation at the break before exposure. However, the HDGEBA/2% CS and HDGEBA /0.5% MWCNT showed less reduction of tensile strength and higher reduce of elongation at break after the accelerated weathering (six months). The overall results of thermal tests for HDGEBA composites exhibited more resistance and improved thermal stability. The glass transition temperature (T_g) values have higher values of DGEBA samples; however, after exposure of accelerated weathering, the HDGEBA composites exhibited more resistance to decrease in the T_g values. The changes on the surface of exposed and unexposed samples were observed by using SEM and the obtained results showed that HDGEBA composites had a smooth surface before exposure while little fractures were shown on the surface after exposure and they are less effective compared to those of DGEBA and DGEBA composites. After exposure of six months, the XRD results showed that the intensity of all epoxy resins and epoxy composites were shifted in angles and reduced compared to those of corresponding samples before exposure. However, the HDGEBA composites showed higher resistance to decrease the intensity with lesser shift in theta angles than the DGEBA composites.

The novelty of the work consists of the using of new epoxy resin (HDGEBA) and its composite to be compared with another epoxy (DGEBA), which are using commonly in industrial and engineering applications. Two epoxy resins evaluated different environmental conditions and are tested by utilising several analysis techniques. The results obtained of this work proved that the HDGEBA and its composites (CS and MWCNT fillers) exhibited more resistant to increase the environmental conditions and improved the chemical degradation, thermal stability, and mechanical degradation compared to that of DGEBA epoxy resin. As the results of the investigation of this work, the HDGEBA and HDGBA composites have a significant impact to be replaced the HDGEBA and HDGEBA composites for industrial application, especially epoxy coating fields.

Declaration

I certify that the ideas, experimental work, results, analyses and conclusions reported in this thesis are entirely my effort, except where otherwise acknowledged. I also certify that the work is original and has not been previously submitted for any other award, except where otherwise acknowledged.

[redacted]

Sameer Awad

2019

Dedication

This thesis is dedicated to the memory of my father and mother, who inspired my dreams and encouraged me to travel far and wide. It is also dedicated to my wife, Eman Khalaf, who supported and sustained my spirit throughout this journey.

Acknowledgements

I want to express my gratitude to my supervisors Assoc/Professor Christopher Fellows, Prof. Trevor Brown, and Dr. Seyed Saeed Mahini for their support and supervision in pursuing this research. They provided me with a global vision of the study during my study. Particular thanks also go to Mr Tony McKinnon, Andrew Wallace, Wayne Dillon, John Pesor, and Malcolm Lambert for their helpful advice, technical guidance and valuable feedback throughout the development of my work, especially with my experiments. I would also like to extend my appreciation and gratitude to the Australian National Fabrication Facility (Qld Node) for DMA tests and Dr. Waael Al-Abdulla from University of Queensland, for managing the facilities of DMA tests. I would also like to extend my appreciation to Mr. John Kuzevski from Brenntag Australia Pty Ltd. NSW, Australia for supplying the epoxy resin type Epalloy 5000 and Dr. Jason Watling of Brien Holden Ltd. NSW, Australia, for the generous supply of the UV treatment chamber. I want to express their gratitude to the Higher Committee for Educational Development in Iraq (HCED) who granted me the financial support for scholarship and University of New England (UNE) for financial support and facilities support. I thank the University of Anbar who granted me a five-year study leave. I would also like to thank the staff at Chemistry Department, School of Science and Technology at UNE for their provision of the experimental facilities and technical assistance. Special and great thanks go to Associate Professor (Rtd.): Warren Halloway in School of Education at UNE for English check and editing. Finally, I wish to express my special thanks to my wife, Mrs Eman Mohammed Khalaf, and my lovely sons, Zaid, Osamah, and Adam for their great encouragement throughout my project and thesis. I am very grateful to my father, who passed away during my study. He was always there with unconditional love and encouragement. I am thankful to my mother, brothers, and sisters for their support and inspiration.

List of Publications

1. **Awad SA, Mahini SS, Tucker SJ, Fellows CM, 2019**. Evaluation of the performance of Microcrystalline Cellulose in retarding degradation of two Epoxy Resin systems**. Journal of Polymer Analysis and Characterisation. 24(2) 150-168:** DOI: 10.1080/1023666X.2018.1562597.

2. **Awad SA, Fellows CM, Mahini SS. 2018.** A comparative study of accelerated weathering of epoxy resins based on DGEBA and HDGEBA. **J. Polym. Res. 25(4):103.** DOI: 10.1007/s10965-018-1489-3.

3. **Awad SA, Fellows CM, Mahini SS. 2018**. Effects of accelerated weathering on the chemical, mechanical, thermal and morphological properties of an epoxy/multi-walled carbon nanotube composite**. Polym. Test. 66:70-7**. DOI: 10.1016/j.polymertesting.2017.12.015.

4. **Awad SA, Fellows CM, Mahini SS. 2018**. Evaluation of bisphenol A-based epoxy resin containing multi-walled carbon nanotubes to improve resistance to degradation. **J. Compos. Mater.** DOI: 10.1177/0021998318816784.

5. **Awad SA, Mahini SS, Fellows CM. 2018.** Modification the protection of the early damage of epoxy resins by using CSW as effective an inhibitor for degradation. **J. of Macromol. Sci. A.** DOI: 10.1080/10601325.2019.1578179.

List of Conference Presentations

1. **Sameer A. Awad, Christopher M. Fellows, Seyed S. Mahini**. Improvement of accelerated weathering resistance of hydrogenated diglycidyl ether of bisphenol A (HDGEBA) by using Multi-Walled Carbon Nanotubes (MWCNTs). International Conference on Nanoscience and Nanotechnology (ICCON 2018), 29 January-2 February 2018, University of Wollongong, NSW, Australia. (**Oral presentation**).

2. **Sameer A. Awad, Christopher M. Fellows, Seyed S. Mahini.** Improvement in Accelerated Weathering Resistance of Epoxy Resin Based on Hydrogenated Diglycidyl Ether of Bisphenol A HDGEBA) Using Calcium Sulfate Whisker (CSW) for Timber Protection. International Conference on Sustainable Fibres, Polymers and Composites, 9th–10th May 2017, the Manufacturing Technology Centre (MTC), Coventry, UK. (**Oral presentation**).

3. **Sameer A. Awad, Christopher M. Fellows, Seyed S. Mahini.** Modification of epoxy resin with Calcium Sulfate Whisker (CSW) to inhibit degradation. World Polymer Congress (Macro 2018), 1-5 July 2018, Cairns, Queensland, Australia. (**Oral Presentation**).

4. **Sameer A. Awad, Christopher M. Fellows, Seyed S. Mahini.** Evaluation of two epoxy systems under accelerated degradation. 36 Australian Polymer Symposium conference. (36 APS), 20-24 November 2016, Mantra Lorne, Melbourne, Australia. (**Poster**).

5. **Sameer A. Awad, Christopher M. Fellows, Seyed S. Mahini.** Improvement of Accelerated Weathering Resistance of Epoxy Resin Based on Hydrogenated Diglycidyl Ether of Bisphenol A (HDGEBA) Using Multi-Walled Carbon Nanotubes (MWCNTS) to Protect Timber Bridges. The 8th International Conference on Structural Health Monitoring of Intelligent Infrastructure (SHMII-8), 5-8 December 2017, Queensland University of Technology (QUT), Brisbane, Australia. (**Conference Paper**).

6. **Sameer A. Awad, Christopher M. Fellows, Seyed S. Mahini.** Effect of accelerated weathering exposure on the properties of timber-adhesive composites. UNE Postgraduate Conference, 17th and 18th January 2017. The University of New England, Armidale 2351, Australia. (**Oral presentation**).

7. **Sameer A. Awad, Christopher M. Fellows, Seyed S. Mahini.** Prevention of the environmental degradation of timber bridges by using two epoxy resins-inorganic material composites. The 9th International Conference on Structural Health Monitoring of Intelligent Infrastructure (SHMII-9), 4-7 August 2019, St. Louis, Missouri, USA. (**Conference Paper presented by Dr. Mahini**).

8. **Sameer A. Awad, Christopher M. Fellows, Seyed S. Mahini.** Cure kinetics, and characterisation of two epoxy resins. UNE Postgraduate Conference “Intersecture of Knowledge”. 15th and 16th January 2019. The University of New England, Armidale 2351, Australia. (**Oral presentation**).

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List of symbols and abbreviations

DGEBA	Diglycidyl Ether of Bis-Phenol A
HDGEBA	Hydrogenated Di Glycidyl Ether of Bis-Phenol A
TMDA	2,4,4-Tri Methylene 1,6-Hexadaimine
MWCNT	Multi-Walled Carbon Nanotube
CS	Calcium Sulfate
MCC	Microcrystalline Cellulose
FTIR	Fourier Transformation-Infra Red
TGA	Thermal Gravimetric Analysis
DSC	Differential Scanning Electron Microscopy
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
NMR	Nuclear Magnetic Resonance
GC/MS	Gas Chromatography-Mass Spectrometry
DMA	Dynamic Mechanical Analysis
ASTM	American Society for Testing and Materials
$\mathbf{T_g}$	The Glass Transition Temperature
PTFE	Polytetrafluoroethylene

Chapter 1: Introduction

1.1. Motivation

In recent years, the use of epoxy resin in composite materials has rapidly increased in many industrial applications, such as bridges, wind energy, aerospace, and sporting goods. However, the rapid degradation of these materials is possible when they are exposed to natural or extreme environmental conditions, which causes serious concern with economic and environmental implications [1-3]. Thus, a significant portion of this study focused on understanding the surface, chemical, thermal, physical, and morphological changes that occur in epoxy resins after they are exposed to different weathering conditions. To protect epoxy resins from degradation and ensure acceptable lifespans in outdoor exposure conditions, different stabilisers were tested as modifiers of epoxy resins [2].

Timber was the material best suited for many Australian infrastructure developments during the 19th and early 20th centuries, and many of these timber structures are still utilised. However, these structures are reaching a critical stage in their lifespans due to their continued exposure to environmental conditions [4,5]. With an increasing focus on the development of durable timber composites in construction systems, the reinforcement of existing timber structures and the use of timber in new constructions is receiving much attention [6-10].

A timber composite consists of timber used in conjunction with other materials, such as epoxy resins [11-14]. Timber has been used as a filler or reinforcing material in composites for thousands of years. The introduction of a natural filler, such as timber particles, in polymers, is appealing to polymer and epoxy manufacturers [15].

The long-term performance of timber composites may be affected by many factors, such as extreme wind events, seismic activities, or environmental conditions. Environmental conditions easily have the most significant impact on the long-term conditions of structural systems made of timber composites and the considerable potential for an economic outcome [16-21].

Timber that is utilised as a structural material and is continuously exposed to different environmental conditions experiences decreased stiffness and strength. Hence, reinforcement of epoxy resins is often necessary to increase the capacity or decrease the flexural deflections of timber [22-24]. However, the lifespan of epoxy resin may be significantly reduced by environmental factors, such as UV light, temperature, and moisture, which may lead to epoxy-timber composites' loss of mechanical and chemical properties [25-31].

Although they have been used since the beginning of the 20th century, timber composites, such as glulam (glued laminated timber), are gaining increasing attention from architects and structural engineers, who see them as attractive materials for many types of structures [32]. However, the properties of glulam are affected by the properties of epoxy adhesives, and epoxy resins can be developed to improve the strength of the glulam. To enhance their mechanical characteristics, such as strength and modulus, glulam products may contain 50% laminated timber if a suitable epoxy resin, such as 10% diglycidyl ether of bisphenol A (DGEBA), and curing agents are used [33–36]. Faherty and Williamson (1999) suggested that the selected resin must be stronger and have greater weather resistance than the timber [37].

At present, the durability of timber composites, such as glulam, that are exposed to the outdoors is not of great concern to the industry [38]. However, with the increasing use of timber-adhesive composites outdoors, the degradation of the epoxy adhesives used in glulam and the interaction between timber and adhesive degradation must be understood [39–43]. An investigation of the adverse effects of exposure to environmental factors on the long-term durability of epoxy resin may clarify the degradation mechanism of resins, leading to improvements in the protection and longer service lives of epoxy resins [44–52].

1.2. Mechanism of Degradation

The weather-related degradation of timber structures and products affects their physical, mechanical, and biological properties [53–58]. The continued degradation of timber composites due to their exposure to different extreme environmental conditions may lead to fractures, failure, and loss of life [59,20]. During the outdoor weathering process, the original timber surfaces become rough, and changes in timber colour may occur as a result of photochemical reactions [60]. Although heat may not be a critical factor as UV light or water, which means as the temperature increases, the rate of degradation increases [59].

The mechanisms of timber degradation suggest that lignin is a critical structure because this component absorbs UV/visible region due to its chromophoric groups [60, 61,62]. Engineered timber composites that contain large amounts of lignin are more susceptible to UV degradation than those that contain negligible quantities of lignin [59,63,64].

Epoxies typically degrade rapidly with prolonged exposure to ultraviolet light, and while some epoxies contain UV inhibitors, these inhibitors only provide limited protection from intermittent exposure to the sun’s light [65]. Outdoor life for unprotected epoxy may be as short as 12–18 months as results of several external environmental conditions such as the direct exposure to the sunlight, the higher temperatures, and moisture [65]. Some epoxies also display changes in the colour when exposed to UV radiation. In addition to inducing chain scission and increasing crosslink density, photo-oxidative reactions may cause the production of chromophoric chemical species [66,67], which may result in the autocatalytic degradation process [50, 59, 68].

1.3. Research Objectives

The objectives of this project are to identify how the epoxy matrix and composite change under the effects of environmental conditions and effectively assess the durability and chemical, thermal, and mechanical properties of the epoxy composite. Preliminary tensile tests on engineered timber have always resulted in the cohesive failure of the timber, so the early stages of composite degradation have not been identified. Therefore, the main focus of this research is the study of neat epoxy resins. How neat epoxy resins (aromatic and aliphatic epoxy resins) behave during long-term aging under different environmental conditions must be understood.

The study seeks to predict the long-term durability of epoxy resins by identifying the effects of accelerated weathering on two epoxy resins (aromatic and aliphatic structures; diglycidyl ether of bisphenol A (DGEBA) and hydrogenated diglycidyl ether of bisphenol A (HDGEBA)). To investigate the effect of accelerated epoxy weathering, various measurements were conducted. For example, Fourier-Transform Infrared (FTIR) was used to monitor the chemical changes of the epoxy, tensile tests were used to follow the mechanical degradation of the epoxy, and thermal tests (Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)) were used to assess the thermal degradation of the epoxy.

Multi-walled carbon nanotubes, calcium sulphate, and microcrystalline cellulose were used to reinforce the two epoxy resins. These fillers were selected because they are considered effective photostabilisers in composite systems. The same tests that were conducted on the epoxy resins without fillers were applied to these systems to see how well the fillers prevented degradation. The results were compared to investigate the improvement of the neat epoxy matrix and epoxy composites' chemical, thermal, mechanical, and surface properties after these materials were aged in various environmental conditions.

1.4. Thesis Structure

This thesis is divided into nine chapters. Chapter Two presents a literature review related to timber-epoxy composites and their degradability issues. This chapter also reviews the research on photostabilising and improving the resistance of filler-modified epoxy to accelerated weathering. Chapter Three discusses the methodology, materials, and epoxy/filler composite preparations as well as the chemical, thermal, mechanical, and degradation testing procedures. Chapter Four covers the chemical changes (carbonyl and hydroxyl groups) caused by accelerated weathering exposure using FTIR spectra. Chapter Five explains the impact of exposure epoxy and epoxy composites to different accelerated weathering periods on the mechanical properties (tensile strength and elongation at break). Chapter Six focuses on the effects of weathering on thermal stability, which was assessed, using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Chapter Seven discusses the SEM tests, which test the effect of accelerated weathering on the morphological properties of epoxy and epoxy composites. Chapter Eight illustrates the XRD characterisations of the epoxy resins and epoxy composites to show their structural changes before and after their exposure to different accelerated weathering periods.

Finally, Chapter Nine summarises all the conclusions of this research and provides recommendations for possible future developments of epoxy composites in outdoor environmental applications.

Chapter 2: Review of Literature

2.1 Overview

A composite is composed of a mixture of two or more macroscopic elements differing in form and the composition of the material, which are principally insoluble in each other [69-77]. Timber-polymer composites such as glulam beams, for example, combine timber and epoxy resins in one composite material [78-80]. Composites also offer excellent resistance to fatigue, and they have low-cost fabrication, and tailored thermal-expansion characteristics compared to those of other materials such as steel and concrete [81, 82]. Combinations of constituent material features make polymer-based composites a subject of tremendous interest in the aerospace, construction, and automobile industries [83-85].

Epoxy composites include many types of epoxy resin and timber, but all are likely to degrade particularly under outdoor conditions, and hence the lifetime of these materials is limited [84, 85,86,87]. Degradation of epoxy composites outdoors is caused by different environmental factors; thus, the collective term “weathering” is used to describe it [88-90]. Photodegradation is outlined as the degradation of a polymeric material generated by photons from highly energetic UV light [91]. A better understanding of the degradation for epoxy resins, particularly in composite materials, is not only of academic attention, but it is also of high practical significance [92-94]. Knowledge of the causes of photodegradation could be utilised to modify stabilisation for producing more stable epoxy composite structures [95,96]. Alternatively, it could be utilised to develop more "environmentally friendly" epoxy designed to disintegrate rapidly outdoors when exposed to daylight but which can maintain its desirable mechanical properties during use under indoor applications [97].

2.2 The Emergence of Engineered Timber

Timber has been utilised widely as a building material in engineering and industrial applications for a very long time. Decreasing supplies of high-quality timber, increasing demands and raising the cost of timber products have been changed from solid-sawn to engineered timbers. They are more efficient for using the available timber resource and are cost-effective [98-100]. The move from solid timber to engineered timber products for construction has increased the use of epoxy resins [101]. Currently engineered timbers are used to produce significant and integral units such as soft timber, ply timber, glued-laminated lumber (glulam), timber I-joists, and oriented strand board [102, 103].

The demand for engineered timber has also grown remarkably and supplied on the same markets as glulam and traditional timber. The consumption of engineered timber has increased annually about 17 % since the 1990s; it was a bit over 3.5 m^3 in 2012. Finger-jointed structural timber is notably cheaper than glulam timber. The price in 2011 was around 290 € when glulam costed around 403 € in 2017 [104].

Engineered timbers are used to generate specific and consistent mechanical properties. Timber alone is a difficult material to work with, compared with plastics and metals that are applied in construction. Engineered timber composites are used in many structural applications and are intended for dry use [105, 106]. However, these materials may be exposed to significant amounts of moisture, temperature, and UV irradiation while in service, which can cause structural failures, shrinkage and swelling for timber in addition to other factors may cause the lumber to warp, deform and twist. However, there are little data in terms of durability and service life of many timber-based composites, which often puts these materials at a disadvantage against other materials [105]. The importance of understanding timber composites has become more significant in improving the building for several reasons, increasing demand, reduce the availability of traditional. The advantages of engineering timber compared to those of solid timber can be listed as follows [105].

1. Enhanced strength and stiffness, because of the changes of these parameters are less than those of solid timber [106].
2. The possibility of corresponing the properties of lamination within the cross-section about the predictable stress levels [106].
3. Providing excellent dimensional stability after exposure to the variations in moisture [106].

2.3 Properties of Timber

Timber as a renewable material has many advantages and a long history of performance under adverse conditions [106-108]. The demand to use timber products for many applications in civil engineering and building fields has increased in recent years. The timber consists of high molecular weight organic compounds such as cellulose, hemicellulose, and lignin, as well as ash-producing materials. It can be collected, sawn, dried and finished to meet the requirements of the industrial and engineering fields [109-113]. Generally, timber contains 30-65 % cellulose, 20-35 % hemicellulose and 15-35 % lignin [114-116].

The timber structure at the cell wall is very complicated because it includes several layers. All plants consist of the primary (P) cell wall layer because it is the basic structural unit of the living cell [117]. The secondary cell wall is thicker than the primary wall and contains three different layers, S1, S2, and S3, from the middle lamella towards the lumen [117]. The central S2 layer is about 1µm thick in early timber and 5 µm thick in late timber and forms the main portion of the cell wall [118]. The S1 layer is between 0.1 and 0.2 µm thick and is the one adjacent to the primary cell wall [118]. Layer the S1 layer consists mainly of a single lamella where the cellulose microfibril [117]. The central S2 layer is about 1 µm thick in early timber and 5 µm thick in late timber and forms the central portion of the cell wall [117]. The inner S3 layer (thickness 0.1–0.2 µm) lies adjacent to the cell lumen and consists of a thin layer of cellulose microfibrils and the timber cell structure as shown in Figure 2.1[118,119].

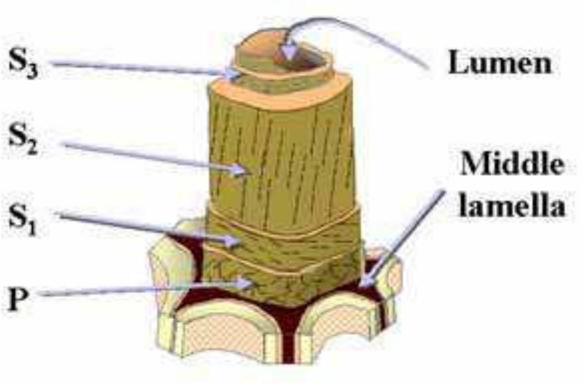


Figure 2.1: Timber cell structure [119]

2.3.1 Cellulose

Cellulose is a linear polysaccharide composed of *β* (1-4) linked with D-glucose units (Figure 2.2). Cellulose highly contains crystalline glucan polymer, which forms the most significant component of the plant cell wall [119]. Cellulose forms approximately 46–55 % in softwoods and hardwoods: 41–48 % in hardwoods and it is located mainly in the secondary walls of timber structure [120]. The molecular structure of cellulose is shown in Figure 2.1[120].

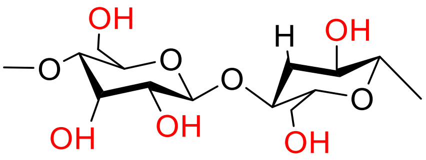


Figure 2.2: Molecular structure of cellulose (cellobiose repeating unit)

2.3.2 Hemicellulose

Hemicellulose is polysaccharides with low molecular weight containing branched chains of xylose, mannose, arabinose, galactose, and glucose molecules [120]. They consist of 20-30% of the timber structure [121-123]. The hemicellulose polymer fills in space in the plant wall and is closely associated with lignin. The hemicelluloses are nanocrystalline and hence more soluble in water and are therefore often eliminated through the pulping method [120]. Figure 2.3 shows the chemical structure of the monomer units of hemicellulose and xylose.

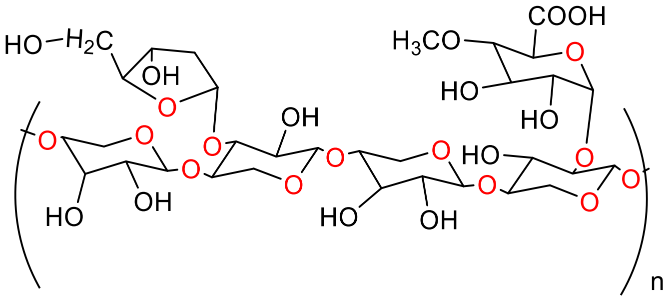


Figure 2.3: The chemical structure of a hemicellulose and xylose units is the monomers in this structure

2.3.3 Lignin

The word lignin was defined by De Candolle in 1819 and is derived from the Latin word, lignum, meaning timber [120]. Lignin is a very complex polymer and consists of phenylpropane units are crosslinked randomly to each other by various chemical bonds [120]. The most important chemical functional groups in the lignin molecule structure include the hydroxyl, aromatic, carbonyl, carboxyl, and methoxy groups [124]. Lignin has advantages that are renewability, sufficient resources, and low cost; it is used as a sustainable energy source [125-127]. Lignin has a greater resistance than cellulose and other structural polysaccharides to most forms of a biological attack. In nature, the degree of polymerisation for lignin is difficult to test because it is continually fragmented during the extraction [128]. The monomer of lignin includes the same phenylpropanoid skeleton, but it differs in the degree of oxygen substitution on the phenyl ring [128]. The H-structure of 4-hydroxyphenyl has a methoxyl group or single hydroxyl, the G-structure of guaiacyl has two, and the S-structure of syringyl has three, as shown in Figure 2.4 [128].

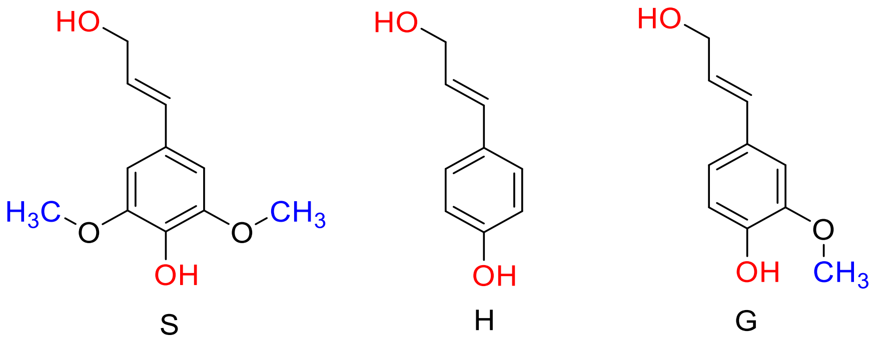


Figure 2.4: Lignin monomer types 4-hydroxyl phenyl (H), guaiacyl (G) and syringyl (S)

2.4 Epoxy Resins

Epoxy resins consist of about 4-6% of the total consumption for thermosets in industrialised countries [129]. Epoxy resins are high-performance thermosetting resins and used as common components by providing a bond between two surfaces. Epoxy resins were made commercially in 1946 [129]. The terms epoxy, epoxy resin, or epoxide describe a broad group of reactive compounds that are characterised by the presence of an oxirane group [130], as shown in Figure 2.5 [130].

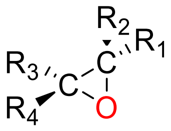


Figure2.4: Epoxide ring of general epoxy resin structures

In the early stage of development, epoxies were presented commercially, and they are now utilised in a wide range of industrial and engineering applications [131]. Epoxies have excellent properties when they are used as adhesives because they have less shrinkage than many other materials [131].

The hot cured means that adhesives require a higher-temperature (~190°C) to achieve the most favourable performance in industrial applications, while cold cured means that adhesives require <70°C to complete curing [132].

The hot-cured epoxy adhesives are a more solid adhesive than those of the cold-cured epoxy adhesives, and they exhibit high moisture, toughness, impact and chemical resistance and having fast cure rates at moderately elevated temperatures [132]. In addition to they have high storage stability, even at ambient temperatures [132]. The applying hot cured epoxy adhesives enhance the elongation and crack resistance and can be improved the hot setting of epoxy resins [132].

Previously, the behaviour of cold-curing epoxies described and discussed, it is clear that there is a pressing need to find reasonable tools to ascertain the curing reactions and the cross-linking degree of commercial cold-cured epoxy-based resins, representing the most frequently used polymeric materials for applications in civil engineering. The durability of these systems, when exposed to environmental agents, also, is strongly connected to their curing reaction. The latter impacts, not only the physical-mechanical properties of the resin but also its performance when reinforced with proper nanofillers, potentially able to improve its properties [133].

2.5 Commercial Types of Epoxy Resins

Epoxies, like all thermosetting resins, are not soluble in water or organic solvents and decompose rather than melt when heated [134]. DGEBA ($n = 0$) is the most common epoxide compound and is used in a variety of commercial products such as paints, adhesives, coatings, and structural applications [135]. Fully cured and cross-linked DGEBA epoxy oligomers with higher molecular weights, produce higher values of glass transition temperatures (T_g). The most common oligomer is $n = 1$ (Figure 2.6) [136].

2.5.1 Diglycidyl Ether of Bisphenol A

Diglycidyl ether of bisphenol A (DGEBA) epoxy is the most widely utilised epoxy resin in industrial applications. Its chemical structure is shown in Figure 2.5. DGEBA epoxies are formed by the reaction of bisphenol A and epichlorohydrin in the presence of sodium hydroxide [136].

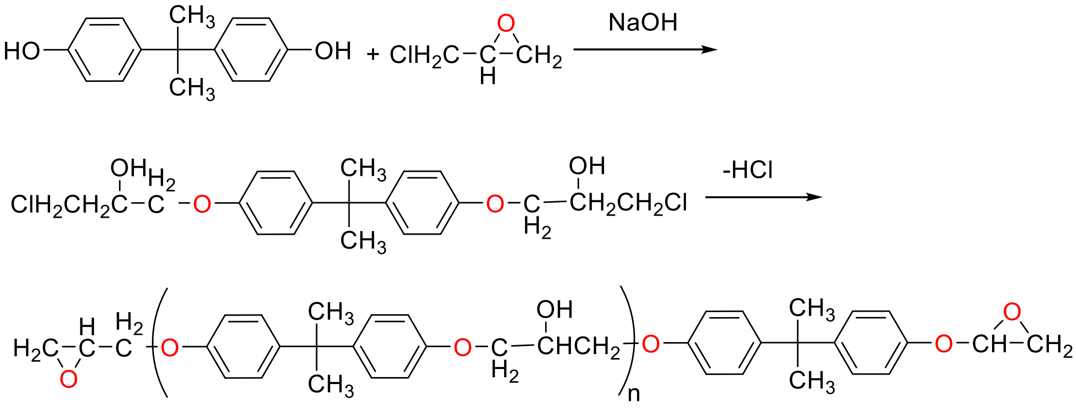


Figure 2.5: The chemical structure of DGEBA-based epoxy [133]

2.5.2 Bisphenol F Based Epoxy Resins

The reaction of bisphenol F (4, 4'-dihydroxydiphenylmethane) with epichlorohydrin produces the bisphenol F based epoxy resin. The chemical structure of bisphenol F based epoxy resins is shown Figure 2.6 [136].

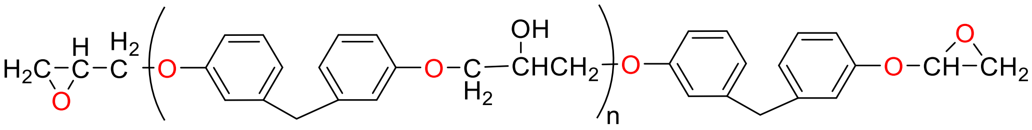


Figure 2.5: The chemical structure of bisphenol F based epoxy resins

2.5.3 Novolacs

Novolacs are epoxidised phenol-formaldehyde or substituted phenol-formaldehyde resins. The chemical structure of Novolacs is shown in Figure 2.7 [136].

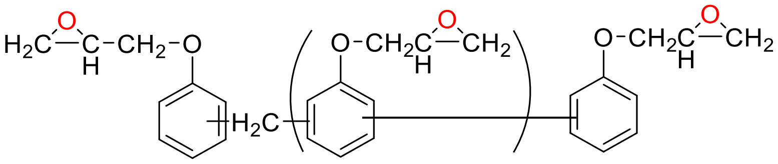


Figure 2.5: Chemical structure of Novolacs

2.5.4 Hydantoin Resins

Recently, hydantoin resins (Figure 2.8) have become popular due to their greater resistance to temperature and stronger mechanical properties, particularly as structural composites. However, this type of epoxy is classified as toxic. At least one hydantoin-based product used commercially necessitates the introduction of specific handling procedures [135,136].

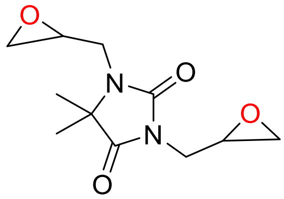


Figure 2.9: Chemical structure of hydantoin monomer

2.6 Curing Agents

Epoxy resins can be cured with curing agents or hardeners to produce three-dimensional insoluble and infusible networks. A variety of types of curing agent can be added to epoxy resins to produce cured epoxy resins[137]. The selection of an appropriate curing agent is dependent on several factors that include the required physical and chemical characteristics, the curing method, and the processing conditions. Epoxy resins can be cured in the presence of catalytic or reactive curing agents [137,138]. The significant role played by catalytic agents or initiators in curing is that of ring-opening homopolymerisation. Epoxy resins can be catalytically cured by Lewis bases such as tertiary amines, or Lewis acids such as boron trifluoride monoethylamine. These catalytic agents act as accelerators in homopolymerisation, or supplement other curing agents, such as amines and anhydrides. A very recent development has been the testing of photoinitiated cationic curing of epoxy resins in conjunction with epoxy coatings from solvent-free and high solid systems [137].

The incorporation of curing agents into epoxy systems contributes substantially to the properties of crosslinked products [137]. To convert epoxy resins to hard, infusible thermoset networks, it is necessary to select the most suitable curing agent to maximise the crosslinking and bonding potential of the epoxy resin [137]. The degree of improvement in the physical, mechanical, and thermal characteristics of an epoxy resin is strongly linked to the choice of curing agent [138]. For example, aliphatic amine curing agents offer superior crosslinking density by improving the physical, mechanical, and thermal properties of the epoxy resin. The selection of a curing agent, therefore, plays a significant role in the curing cycle of the product, in terms of curing kinetics, time to gel, degree of curing, viscosity, and the final characteristics, such as enhanced resistance to fractures. [137,138]

2.6.1 Amine Curing Agents

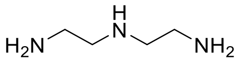
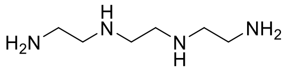
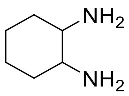
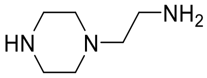
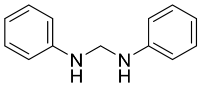
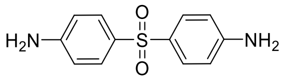
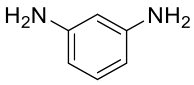
Primary and secondary amines are generally considered the most reactive curing agents, whereas tertiary amines are classed as catalytic [139]. Diethylenetriamine and triethylenetetramine, which are classified as more reactive primary aliphatic amines, can produce cured epoxy resins at room temperature [135,140].

Amine cured systems, however, tend to produce high exotherms in curing epoxy resins and the use of modified aliphatic polyamines results in lower toxicity, reducing exotherms in large castings, and improving flexibility [130]. For example, of the piperidine reacts efficiently in rubber modifications of epoxy resins [139] and polyamides can be utilised in any ratio to balance thermal and mechanical characteristics [130].

Aromatic amine is a weaker base than aliphatic amine and takes longer to cure at room temperature due to steric hindrance from the aromatic ring [141]. In practice, aromatic amine usually requires a two-step curing, the first step is performed at a low temperature of approximately 80°C to reduce heat generation, while the second occurs at a higher temperature in the range of 150°C to 170°C [141]. Aliphatic and cycloaliphatic amine are employed as curing agents for low-temperature epoxy systems, such as adhesives and coatings, while aromatic amine curing agents in the production of matrices for fibre [141].

Although numerous compounds are reactive toward the epoxy group, amines and anhydrides are the most commonly used curing agents. A range of aromatic and aliphatic amines may be used for curing epoxy resins [141]. The cured properties of the resins are related to the nature of the amines used. Aliphatic amines offer ambient curing temperatures and low viscosity. The cured resins have formidable physical properties, retaining these for extended periods at temperatures of up to 100 °C, as well as excellent chemical and solvent resistance. [141]. The variability of these properties is controlled by the mixing ratio. However, the toughness of the final cured resin is rated as low [141]. Cycloaliphatic amine curing produces greater toughness than aliphatic amine curing [142]. Cycloaliphatic amines show lower reactivity toward epoxies than acyclic aliphatic amines [142], implying that the former systems require a longer pot life [142]. Aromatic amines are less reactive than aliphatic and cycloaliphatic amines due to the delocalisation of electrons [142]. Thus, these systems also require a longer pot life and elevated temperatures for curing, but produce resins of a superior chemical and thermal resistance compared to aliphatic and cycloaliphatic amine-cured resins. Additionally, they retain their properties at temperatures as high as 150 °C for longer durations [142]. The most common commercial amine curing agents are listed in Table 2.1.

Table 2.1. Some commercial amine curing agents [130]

Chemical formula	Name
	N1-(2-aminoethyl) ethane-1,2-diamine
	Triethylenetetramine
	1,2 di - amino cyclohexane
	N-amino ethyl piperazine
	Methylene di aniline
	4,4'diaminodiphenylsulfone
	*m* - phenylenediamine

2.6.2 Acid /Anhydride Curing Agents

The acid/anhydride curing agents show lower exotherms on the cure and cause a lower sensitivity to the skin than those of other aliphatic cured amine systems. In practice, anhydrides are preferred to acids since the following release more water on curing, leading to foaming of the product [137]. Numerous structurally different anhydrides can be utilised as epoxy curing agents [137]. The most significant commercial anhydrides as curing agents are phthalic anhydride and tetra hydrophthalic anhydride [130,137].

2.7 Curing Reactions of Epoxy Resins

The selection of curing agent is a critical parameter. Epoxy resins can be converted to a thermoset state by a chemical reaction (curing) between the resins and curing agents such as 2, 4, 6-trimethylene-1, 6-hexadamine (TMDA). The cured epoxy resins react at room temperature or need higher temperatures [137]. By incorporating the curing agents, the epoxy resins are converted into solid, infusible thermosets networks. An epoxide with one or more curing agent (a hardener) are transformed from low-molecular-weight molecules into a highly cross-linked structure [132]. This will create polar hydroxyl groups from the epoxide ring-opening reaction [137]. As the commercial epoxy resins having a higher curing reaction, they can modify the characterisations of epoxies such as thermal stability, viscosity, cross-link density, the resistance of solvents and chemical materials, flexibility and adhesion, and mechanical properties [137]. The epoxy resins and curing agents are selected based on a variety of factors such as viscosity, curing temperature, ultimate mechanical, thermal, chemical, electrical properties, toxicological, environmental limitations, and the cost [143]. The ratios of epoxy resin and curing agents have a significant impact on the structure and the properties of cured epoxy resin. The high level of crosslinking and the nature of interchain bonds give cured epoxy resin many desirable characteristics [65].

The curing reaction is typically carried out at a temperature range from 100 ºC to 200 ºC. Curing reaction requires that an epoxide group reacts with a primary amine group to link secondary carbon atom with the nitrogen atom and yield a hydroxyl group and a secondary amine group. Also, another epoxide group reacts with a secondary amine to produce a tertiary amine [144].

The curing reaction mechanism between epoxide and amine to form the network cured epoxy structure is shown in Figure 2.10 [145].

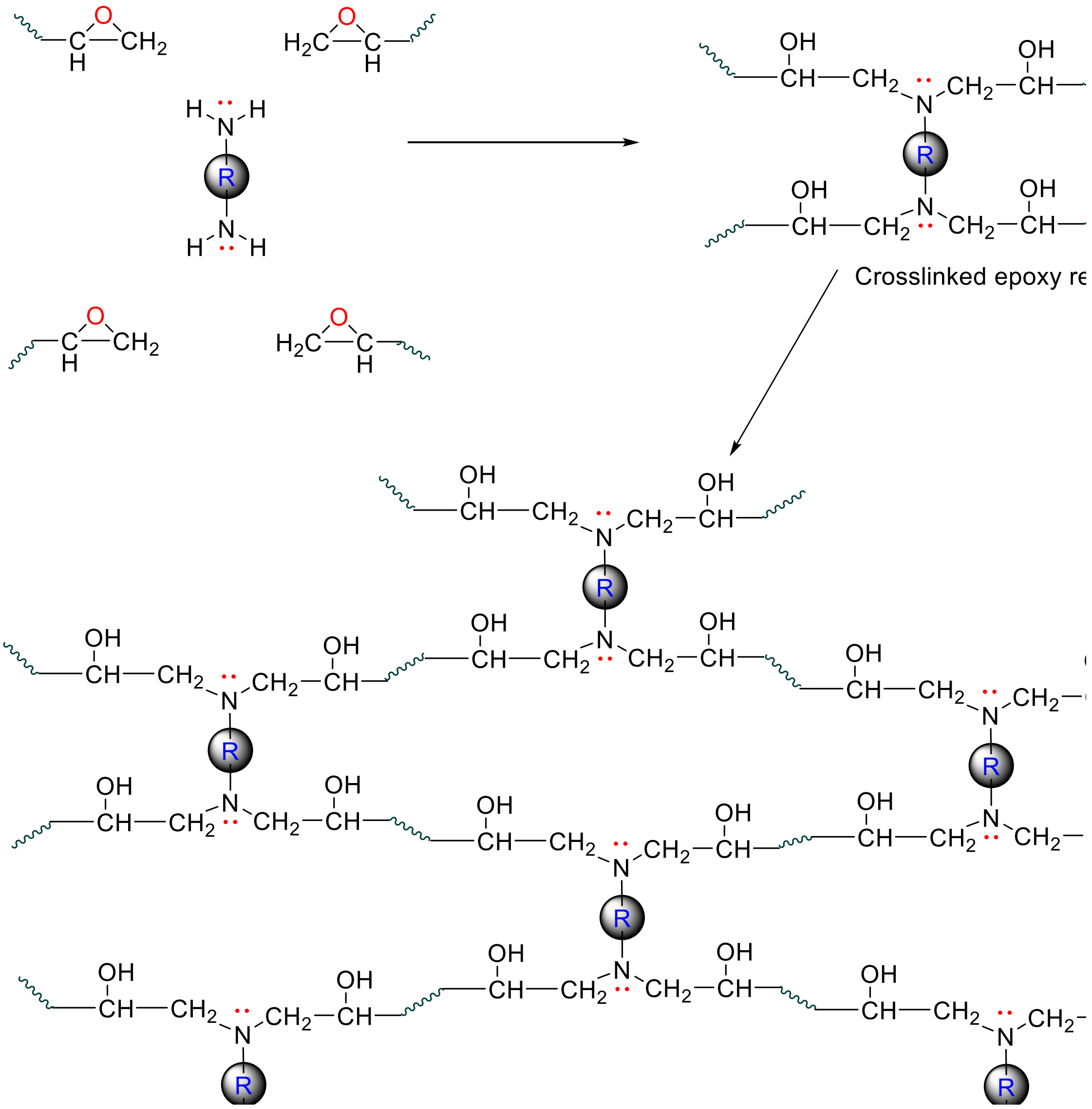


Figure 2.7: Mechanism of reaction between the curing agent and epoxy resin to formation cured epoxy [145]

2.8 Applications of Epoxy Resins

Epoxy is one of the main classes of structural and engineering resins used in human life applications and has high-performance bonding strength [139]. Also, the epoxy resin can be modified to apply for many applications such as for metal, glass, and plastics because of having excellent adhesion to various substrates such as distinct chemical and corrosion resistance. They have high tensile, flexural strengths, thermal stability, and excellent electrical insulation. [143, 144].

2.8.1. Adhesives

Cured epoxy adhesives have excellent bonding features. Often, the curing reaction between epoxy resins and curing agents can be formed at the room temperature (without heating). Epoxy adhesives may be utilised to bond metals, rubbers, timbers, ceramics and glass materials with acceptable results [146-148]. As the chemical structure of epoxy resins having higher molecules weights, they lead to improving the adhesion strength and chemical bonding between the molecules, thus supporting the mechanical properties and thermal stability of epoxy resins [147]. Now, the bonding of timber–timber with epoxy adhesives is very successful and can be utilised extensively in the aircraft and automotive applications [149-151]. The world capacity of producing of epoxy adhesives began since the 1980s and reached to around 600 000 tonnes per annum. However, by the late 1990s, the world market for epoxy adhesives had risen to about 750 000 tonnes [152]. Thus, the global consumption for thermosetting plastics and epoxy resins reached to about 10 million tonnes per annum [152].

2.8.2. Coatings

Epoxy coatings are one of the most important types and are utilised in a broad range of common industrial applications such as synthetic tank lining, the inner surfaces in beer cans, and some auto paints, particularly those on vehicles [152]. Epoxy coatings are durable and have excellent adhesion. They represent the optimum option in many aircraft applications because of having low shrinkage and release of volatiles during the curing, high strength, and excellent durability in hot and moist environments [153]. However, the performance of clear coatings on timber has generally been so poor, which they are not recommended for the finishing of exterior timberwork unless regular and costly maintenance is carried out [154].

2.8.3 Laminates and Composites

The epoxy composite and laminated materials display an excellent bond during the cured process with low shrinkage [154]. They provide high chemical, thermal, mechanical properties and resistance to moisture. They are used in the construction applications and are joined in concrete, metal, flooring, and timber [153]. Laminating adhesives are utilised with different reinforcements such as timber, glass fibres, synthetic fibres, graphite, and Kevlar fibres [153]. Applications of laminates include aircraft, missiles and structural components, chemical resistant tanks, laminated tubes and pipes for conveying oil [153,154,155-157].

2.9 Weathering of Timber

Weathering is defined as the aging which occurs in the service when the materials are exposed to the combination of environmental elements such as sunlight, rain, air, snow, brine or freezing [158, 159]. Weathering can cause the failure of the materials [91,159-162].

When exposed the timber to the environment, unprotected timber suffers rapid surface degradation due to ultraviolet light (UV), temperature, and humidity [159]. Over the time, these factors will change the main structure of the timber [163, 164]. The chromophores in timber are reported to absorb UV light with a maximum wavelength at 280 nm and reducing the absorption with further wavelength up to 380 nm into the visible region of the solar spectrum [165].

Timber has the ability to absorb light and can be attributed to a broad range of chromophoric groups primarily associated with lignin [162]. Some polyphenolic lignin exhibit variable degrees of sensitivity toward the light, depending on mainly intensity and energy distribution of light. For instance, when the timber absorbs UV light, it produces singlet oxygen or free radicals at the chromophoric sites, which then initiate a series of free radical and oxidative photolytic degradation reactions [166-170]. Therefore, the location and nature of chromophores in the lignin structure consider more critical in determining the rate of photodegradation of timber [165]. Figure 2.11 illustrates the UV absorption spectra of weathered and control timber.

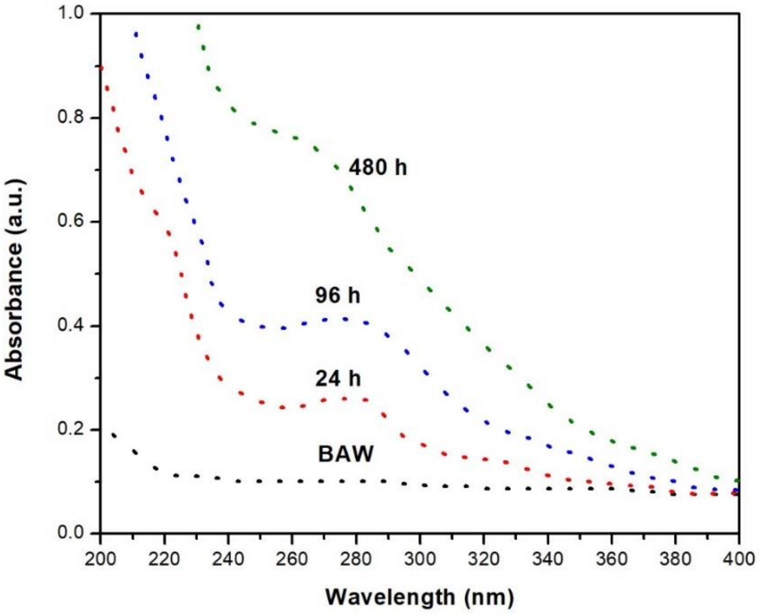


Figure 2.11: UV absorption spectra of weathered and control timber [171]

The photodegradation of timber as a result of exposure to outdoor weathering conditions is difficult are not repeatable [172]. Therefore, the light-induced degradation of timber is usually investigated under artificial conditions [173]. Many studies were utilised the artificial light source of timber degradation was (UVA, 290-400 nm) [174].

Cellulose has less impact than lignin when exposed to the degradation factors except for oxidation in the top surface layer [108]. The degradation of cellulose by UV light is caused by a loss of mass, a decrease of cellulose content and the polymerisation degree [162]. The photodegradation mechanism of cellulose and hemicellulose are based on the energy distribution and the intensity of the sunlight. For example, shorter wavelengths around 280 nm lead to a hydrolytic chain cleavage and create aldehyde groups while longer wavelengths around 340 nm cause degradation in the presence of oxygen to produce peroxide groups [162,164]. For the photolytic degradation of cellulose, the cleavage of carbon-oxygen or carbon-carbon bonds will require an energy level corresponding to wavelengths of 340 nm or shorter [170]. Lignin is a good absorber and is accomplished of autoxidation. For these reasons, Lignin retards the photolytic degradation of cellulose because lignin is a good absorber and more accelerated of autoxidation [172]. Many research works were investigated the mechanism timber weathering mechanism and they were obviously revealed that the absorption of a UV photon could produce a free radical formation and the hydroperoxide is formed as result of the action of oxygen and water [172]. The degradation of timber produces a series of chain scission reactions and create free radical and hydroperoxide [173]. A proposed mechanism showed that the compositions of timber at the surface initially absorb UV light, and then an energy converts from a molecule to molecule dissipates excess energy to produce new free radicals [174]. In this way, free radicals migrate more in-depth into the timber and cause photodegradation reactions [104]. After prolonged exposure times, the content of lignin through the thickness of timber modifies gradually even after the degradation of the surface layer, with less lignin at the surface and more in the centre portion [175]. Figure 2.12 displays the photodegradation mechanism of timber and Figure 2.13 illustrates the photo-oxidation pathway of lignin.

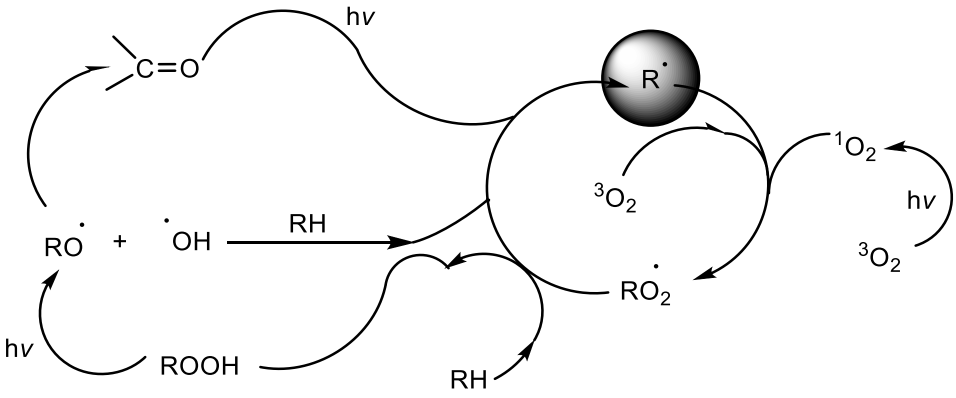


Figure 2.12: Mechanism of Photodegradation of timber [170]

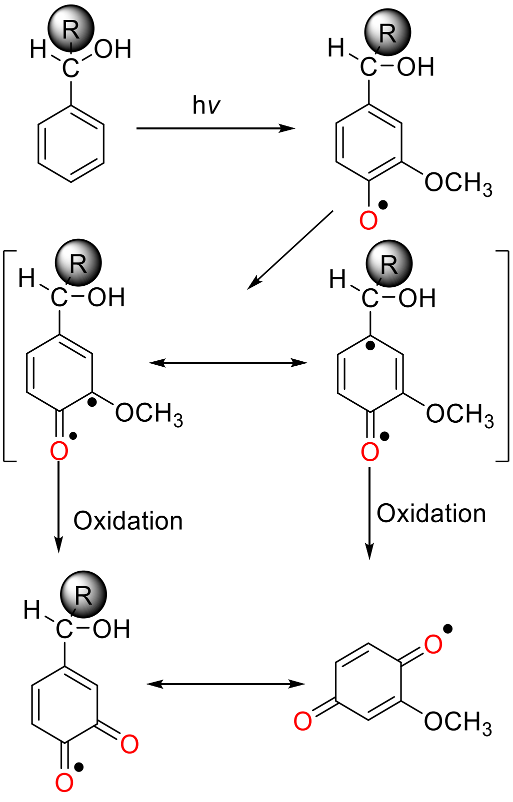


Figure 2.0: The lignin photo-oxidation pathways [175]

2.10 Water and Temperature Effect on Timber

Water is considered to be a critical element and contributing to timber degradation when subjected to outdoor applications. Timber absorbs moisture in the humid atmosphere and when immersed in water causes swells as a result of the higher content of moisture which creates cracks in the timber matrix and contributes to the loss of properties such as mechanical properties (strength and modulus) [175]. Moisture degrades the timber interface and decreases stress transfer efficiency from matrix to timber [104]. The higher water uptake of timber can lead to poor adhesion and forming voids between the molecular chains, thus causing the degradation [175].

Hydroxyl groups in the timber are responsible for the absorption of water and dehydration, which leads to the shrinkage by about 1.2-4% [176]. The shrinkage and swelling of timber create as a result of the response of moisture and leads to joints to open and mating portions to acceptable together poorly. To minimise the shrinkage of getting better properties of timber adhesives, it requires to reduce the moisture from the contents of timber [176,177,178].

The temperature is the most significant factor that causes the degradation of timber; the rate of photochemical and oxidative reactions increases as the temperature increases [179]. The changes in temperature induce a thermal gradient between the surface layer and the inner layer of timber materials, which can lead to the formation of cracks [180, 181]. The formation of cracks is accompanied by a loss of strength and an increase in the timber porosity of timber, which may lower the chemical resistance of the timber [182]. Williams (2005) confirmed that singlet oxygen quenchers could prevent the formation of hydroperoxides, stabilising timber against photodegradation [171].

2.11 Environmental Degradation of Epoxy Resins

Properties of epoxy resins are affected by several external environmental conditions such as temperatures, moisture, and sunlight [1, 104]. Many epoxy resins are prone to photochemical degradation, that is caused by ultraviolet solar radiation and atmospheric oxygen, which lead to chain scission of the polymer backbone. Chemical degradation processes can have physical origins such as being caused by mechanical stress, heat or light [1,183]. The susceptibility of epoxy to degradation depends on its structure on its molecular weight. Epoxies and chains containing aromatic functionality are especially susceptible to ultraviolet degradation while hydrocarbon-based polymers are susceptible to thermal degradation and are often not ideal for high-temperature applications [184]. Furthermore, epoxies, which consist of lower molecular weights, are more susceptible to degradation [1].

Also, the combined conditions of heat, water, and sunlight are expected to have the greatest impacts on the surface, where abundant supplies of oxygen and water are present [184]. Therefore, a suitable method for following the degradation mechanisms would be one which investigates chemical changes on the surface and observing the penetration rate into the bulk of the epoxy resins [184]. For example, oxidative degradation is one of the chemical changes that are observed on the epoxy resin surface [185-187]. It is widely noted that during the amorphous of epoxies or polymers, the molecules of UV stabiliser are dissociated to the amorphous region and therefore the crystals of polymers or epoxies remain without protection. In the amorphous region, the reactions of degradation are producing carboxyl end groups which are not expected to take place because of the presence of oxygen starvation and the trans conformation of the molecules within the amorphous region which do not lead to carboxyl formation [188]. The water and oxygen permeate easily in the amorphous regions of some polymer and epoxies and cause degradation [172].

2.11.1 UV Light

The epoxy resin in timber composites is also exposed to attack by incident sunlight. Aromatic epoxy adhesives are more easily degraded by UV light [189]. All aromatic groups in the structures of epoxy resins absorb sufficient UV radiation to create bond dissociation [1,190-192]. Some polymers and epoxies absorb UV photons and produce photooxidative reactions which change the chemical structure [3]. The chemical reactions of epoxy resins usually produce molecular chain scission or chain crosslinking, as shown in Figure 2.14. Chain scission of epoxy resins decreases the molecular weight, the strength and heat resistance [191]. Chain cross-linking may lead to excessive brittleness and can cause microcracking [190]. Some epoxies exhibit a colour change when exposed to UV radiation. Furthermore, the chromophoric species are induced as a result of the increasing of crosslink density, photo-oxidative reactions. [193-195]. The photodegradation of epoxy resins occurs when they are exposed to the cracking of the surface with a loss in the stiffness and strength. The initial step in the photodegradation of adhesives involves photoabsorption at a particular wavelength, which depends on the structure of the resin and the presence of impurities. Epoxy resins do not have pi bonds; but - this is not true. They frequently have aromatic groups with C=C bonds. So, this is not the reason they are not expected to absorb at wavelengths above 190 nm. Epoxy resins have molecules that contain C-H, C-C, C-N, C-O and C-Cl bonds; hence are not expected to absorb wavelengths longer than 190 nm. Short wavelength photons absorbed by central structural components can cause severe degradation, such as bond scission [194]. Free radicals, however, are formed after adhesives are irradiated with UV light of wavelengths less than 300 nm. Epoxies can be degraded via a photo-oxidative pathway or photolytically. In the latter, epoxy resins contain chromophores which absorb UV light directly, without first undergoing oxidation reactions. For example, aromatic polymers absorb only a small portion of the radiation that causes photochemical changes [196-198]. A free radical reaction mechanism is suggested in Figure 2.14 for epoxy degradation in supercritical 1-propanol [199].

The elimination of water from the secondary alcohol group was the first reaction when the epoxy resin was heated and produced allylic bonds, aromatic ether linkages, and experienced homolytic cleavage [199]. The free radical one was saturated with active hydrogen from 1-propanol to yield a Bisphenol-A radical 4, 4-(cyclopropane-1, 1-diyl) diphenol. Then Bisphenol A also underwent homolysis and formed free radicals. The two free radicals could capture hydrogen from the neighbouring methyl in free radical to generate phenol and 4-isopropenyl phenol [199]. Woo et al. (2007) exposed a DGEBA epoxy reinforced with 3% organoclay to up 2000 h accelerated weathering, the environmental condition was set at 42±3 ºC, and 30±5%RH and the wavelength of UV lamps was 340 nm [200]. They have investigated the effect of the photodegradation by FTIR and found that the carbonyl index of epoxy and epoxy nanocomposites increased as the UV irradiation exposure increased up to 2000 h. Some researchers examined the impact of UV exposure on the properties of epoxy filled nanoclay and carbon nanotubes. They reported that the addition 0.5% nanoclay into DGEBA epoxy displayed possibilities of reducing the degradation processing [200-203]. Peng et al. (2018) investigated the effects of UV irradiation (UVA-340nm) on the mechanical properties of cured DGEBA epoxy. The epoxy samples were exposed to UV irradiation up to 543 h. They stated that no significant changes in mechanical and electrical properties in the early stages of the exposure times. However, after exposure to 303 h and 543 h, electrical and mechanical properties decreased significantly [204]. Another work reported the effect of the UV irradiation (UVB-330 nm) on the thermal properties of cycloaliphatic epoxy. They concluded that the exposure to UV irradiation for a longer time reduced the thermal stability [205].

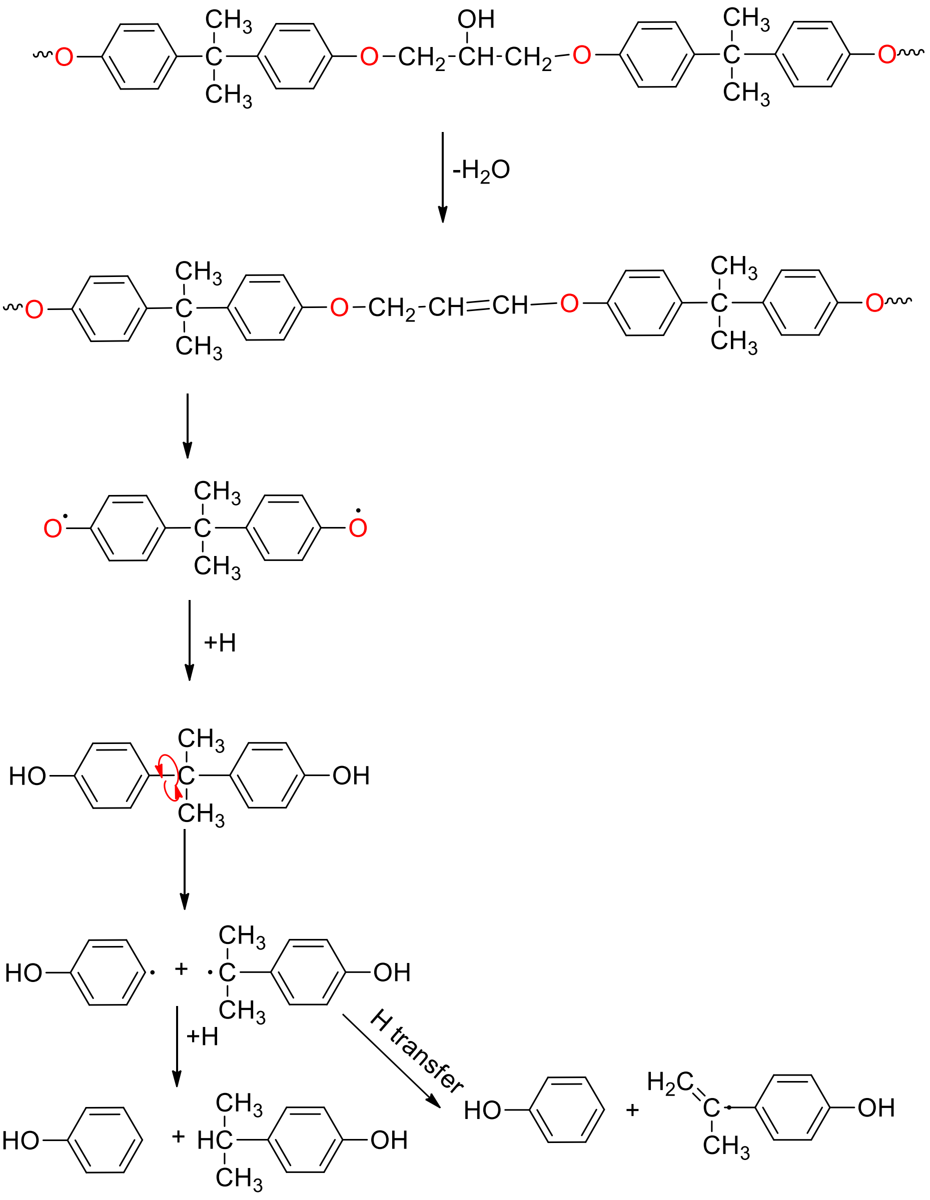


Figure 2.14: Photodegradation mechanism of cured epoxy [199]

2.11.2 Oxygen

Atmospheric oxygen causes oxidation of epoxy materials, and this is sharply accelerated by UV irradiation, elevated temperatures and by the presence of specific impurities that catalyse the oxidation process [206]. The degradation products that are formed by the presence of oxygen are alcohols, hydroperoxides, lactones, esters, carboxylic acids, ketone, carbonyl and olefinic groups [205]. Hydrocarbon-based adhesive formulations that contain double bonds are especially susceptible to oxidation [205], whereas another study determined that tertiary carbon atoms are most vulnerable to attack in epoxy resin structure [206]. The oxidative degradation of saturated (aliphatic structure with single bonds) epoxy resins occurs very slowly in the presence of oxygen, and the reaction is autocatalytic, while unsaturated (aromatic structure with double bonds) epoxy resins undergo oxidative degradation much more rapidly as a result of complex free radical processes involving peroxide and hydroperoxide intermediates [206]. Singlet oxygen has a negligible concentration in the atmosphere. However, there are several sources to produce it, such as decomposition of ozone, which reacts with unsaturated carbon-carbon bonds to generate hydroperoxides [207]. Carlsson (1990) investigated the photodegradation of a range of hydrocarbon epoxies and found it was not a function of their tendency to absorb light; instead, it is a function of their susceptibility to oxidation such as methylene groups in epoxy resin or polymers [208]. Antioxidants were used to prevent the oxidation reactions of epoxy resins formulations[209]; however, another study suggested that antioxidants are not capable of stopping oxidation reactions entirely by preventing the formation the free-radicals [209]. The higher temperature and moisture cause high oxidation of epoxy resins compared with that of epoxy with antioxidants [209]. Another study found that the reaction rate near the surface of DGEBA epoxy could be exposed to UV irradiation with longer time is very high and most of the oxygen is consumed before it can penetrate far into the material [210].

2.11.3 Moisture and Water Exposure

Epoxy resins can absorb moisture up to 7% of their mass on exposure to humid environmental conditions [210, 211] with adverse effects on the overall properties; chemical, mechanical, thermal and physical characterisations. Moisture decreases thermal stability and reduces the glass transition temperature, T_g of the timber/epoxy composites [212-214]. Moisture can cause swelling and weakness of epoxy adhesive joints, depending on the type of epoxy resin and the exposure conditions [201,213]. Water diffuses into the epoxy structure, which causes swelling and physical changes such as plasticisation and hydrolysis. Epoxy resins are relatively polar compared with thermosetting polyester because they contain ether groups, C-N bonds, and hydroxyl groups. Many studies investigated that absorbed water mostly located in the hydrophilic part of the epoxy matrixes and caused irreversible swelling [214-218]. Vanderwel et al. found that the water absorption is caused by the hydrogen bonding between water and polar groups were common in the hydrophilic epoxy coating, and the absorbed water induced the swelling of the cross-linked epoxy and weakened the mechanical property of the epoxy coatings [219].

In the presence of water/moisture, timber is prone to absorb a significant amount of water and swells; epoxy, due to the highly cross-linked structure, can absorb lower amounts of water, with minimal swelling. As a consequence, stress at the interface epoxy/timber arises, with a consequent loss of adhesion [217].

Some researchers have suggested that absorbed water can attack the epoxy/filler composite interface and cause debonding at the interface [220,221]. Water permeability is highest for epoxy resins compared to corresponding thermosetting polyesters, and this can cause both reversible and irreversible damage to the epoxy composites. Plasticisation is generally a reversible process based on desorption of the moisture while hydrolysis of chemical bonds for methylene groups will convert to esters, a carbonyl group, amide, or ethers that causes irreversible damage [222-224]. Most commercial epoxies are formulated with inorganic fillers such as clay or silica, or with carbon fibre. They are applied to improve properties and reduce cost [225, 226]. Ekin et al. investigated long-term absorption exposure (9 months) on the behaviour of epoxy resin /nanosilica composites. The results of this study displayed that the kind and particle size of the filler has no significant impact on the percentage of water absorption of epoxy matrix composites [227]. The rate of water absorption values fluctuated, and the averages of these values obtained between 1440 and 6480 h were 0.87% and 0.95%, for bisphenol A-based epoxy resin while the epoxy nanocomposite was about 0.83% and 0.85% [227].

Singh et al. investigated the exposure for DGEBA epoxy and epoxy-nanoclay composites to constant relative moisture conditions (50 ℃) in a temperature-moisture chamber. Both neat epoxy and epoxy-clay composite samples gained mass due to moisture uptake. They noticed that after the first exposure to up to 250-325 hours of moisture condition, the mass gain increased by 1.6%. With further exposure times, the epoxy resin continued to increase compared with epoxy-nanoclay composites that the increase was minimal [228]. The final mass gain at 4770 hours of moisture exposure, for epoxy-nanoclay composites, was 2.0% while the DGEBA epoxy gained 3.4% as shown in Figure 2.15 [228].

Ramirez et al. exposed carbon fibre/DGEBA epoxy composite to saltwater and distilled water at 40˚ and 60˚C and found a decrease in (T_g up to 19 ℃), a 50% decrease in the flexural strength, 25% decrease in the strength, and an 18% decrease in the modulus [229].

Mourad et al. (2010) also noticed no significant changes in tensile strength or modulus in glass/epoxy composites after one-year exposure to seawater at 23 ℃ or 65 ℃ [230].

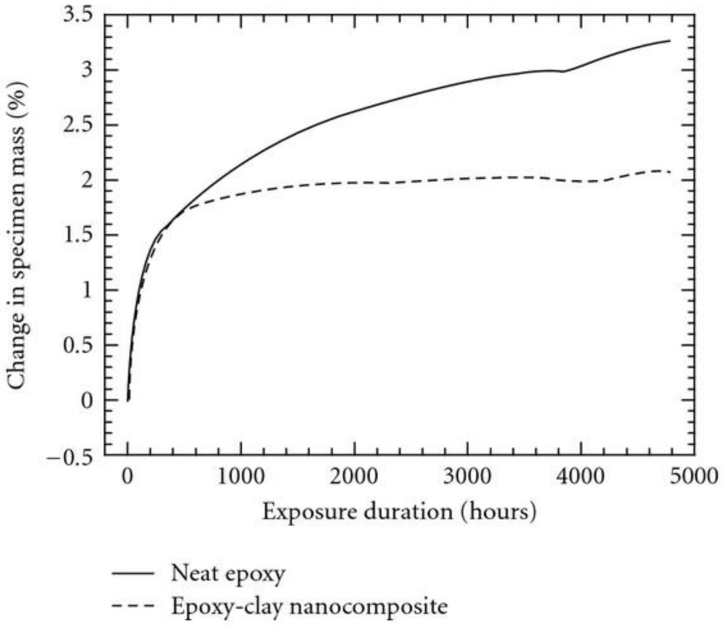


Figure 2.15: The average of moisture uptake for epoxy resin and epoxy-nanoclay composites [228]

2.11.4 Effect of Temperature

The physical properties of epoxies are highly sensitive to the impact of temperature. Increasing the temperature produces a decrease in elastic modulus, reducing tensile strength, and an increase in ductility [231-233].

The T_g values of epoxy can be decreased as a result of the exposure to moderate temperatures as a result of not fully cross-linked thermoset epoxy can promote their post-cure. The post-cure is usually reflected in an increment of T_g, strength, and stiffness of the resin [234-236]. However, T_g values never exceeding 75 °C are generally found for an epoxy/aliphatic amine couple, even if the cross-linking of the resin has been completed through a post-cure procedure [235].

Besides the physical aging of hot cured epoxy resins, physical aging can also take place in cold-cured epoxy resins, which causes a reduction in the free volume of epoxy resins over time, that is, in densification, with consequent modification of all of the mechanical, temperature-dependent properties [237]. Physical aging in the glassy state is prolonged. However, it proceeds rapidly at temperatures close to T_g. This latter is the case of cold-cured resins, in which T_g can be easily approached and even exceeded by the external temperature [237]. Physical aging is a thermoreversible phenomenon, which can be erased when the polymer is heated above its T_g [237]. When the service temperature exceeds T_g of aged adhesive resins, a transformation of the resin takes place, and the initial properties are recovered [237]. Cold-cured epoxy resins exposed to natural weather, therefore, are regularly subjected to aging and rejuvenation processes that take place in nonisothermal conditions, depending on the actual meteorological weather [236].

Thus, the changes in temperature can cause long-term degradation in some epoxy resins, depending on the epoxy structure [238]. Parvatareddy et al. exposed a titanium oxide-epoxy resin composites to three different temperatures, 150, 177 and 204 ºC, the results displayed that the highest exposed temperature which was approximately 204 °C, caused the greatest loss in the mass and the rate of strain reduced by 10-20% after exposure to six months weathering [239]. Wolfrum and coworkers [240] attempted to rapidly evaluate thermo-oxidative effects in graphite/epoxy laminates using exposures at up to 200 ºC for 450 days. Under these conditions, oxidation is much more severe at the composite surface, although changes in the infrared spectrum were observed even 500 µm below the surface. They reasoned that since carbon fibres do not absorb moisture, absorption took place at the interface possibly through cracks. Karbhari et al. exposed carbon/epoxy-confined concrete cylinders to freeze-thaw cycles between 20 ºC and -18 ºC for 45 days and stated a decrease in the compression strength of about 5% and significant drops in overall stiffness [241].

Soudki and Green exposed a minimal number of carbon/epoxy-wrapped concrete cylinders to freeze-thaw cycles between 18 ºC (for 8 hours in water) and -18 ºC (for 16 hours) and concluded that the exposure caused a more catastrophic failure, with specimens showing evidence of microcracking. The single-layer wrap samples showed a loss about 17% in axial compressive strength caused by this level of exposure [242].

2.12 Photostabilisation

The compounds which are utilised for the retardation and elimination of the photochemical process in epoxy or polymers are usually referred to as stabilisers. The first idea of attack to improve the resistance of epoxy-timber composites is often to add photostabilisers [243]. They are generally classified according to the mechanism of degradation they hinder [244]. Ultraviolet absorbers (UVAS) and free radical scavengers consider important photostabilisers for polyolefins. Readily available commercial UVAS are benzophenones and benzotriazoles and hindered amine light stabiliser HALS (2, 2,6,6-tetra-methyl-piperidine) [1, 245].

Photostabilisers are additives to polymeric or epoxy materials which prevent photodegradation or crosslinking caused by UV light [1]. Stabilisers are usually more compatible with the amorphous part of epoxy resins [246, 247]. Any degradation by UV radiation is near to the surface of material because of the reduction of light with increasing substrate depth [248]. Therefore, the concentration of UV light irradiation can be detected at a depth of 400 to 500µm for aromatic skeletal vibration (1510 cm^{-1}) and at a depth 600 to 700µm for carbonyl vibration (1710 cm^{-1}) under long-term condition [248]. The radiation filtering effect of UVA increases logarithmically with its concentration according to the Lambert-Beer law. Also, any additive (photostabilisers, antioxidant, a thermal stabiliser must be evenly distributed with the epoxy, which requires it to be compatible with the epoxy resins [249].

As oxygen diffusion is higher in the amorphous region of epoxy resin, photo-oxidation reactions will be higher in the amorphous areas of polymers or epoxies so that it is good that the stabiliser is concentrated there [250]. Inorganic UV absorbers such as ZnO and TiO_2 have broad absorptions in the UV and visible ranges while organic UV absorbers only absorb specific wavelengths in the UV range with almost no absorptions in the visible range [251-253]. Pigments and UV absorbers have been used with some success in mitigating changes that occur during timber-polymer composites weathering [254]. Pigments were shown to reduce the increase in lightness and significantly increase the flexural property retention of timber-polymer composites after accelerated weathering [254]. Lundin (2001) investigated the effect of hindered amine light stabiliser (HALS) content on the performance of timber-polymer composites [255]. The author reported that the addition of HALS to the composites did not affect colour change caused by accelerated weathering and slightly improved the mechanical property retention [255]. Stark and Matuana (2003) examined the effect of a low molecular weight HALS, a high molecular weight HALS and pigment on the changes in lightness and mechanical properties of timber-polymer composites after weathering. Pigments significantly reduced composite lightening and loss in mechanical properties. Regardless of molecular weight, HALS was found to be ineffective in protecting the composite against surface discolouration and flexural property loss [256].

2.13 Improved Performance of Epoxy Resins

In recent decades, much work has been dedicated to strategies for minimising brittleness and improving elasticity and mechanical strength, while simultaneously maintaining the thermal stability and chemical resistance of epoxy resin-based materials [257,258].

The developments of timber-epoxy composites with nanofillers are one of the most promising approaches in future industrial applications and civil engineering [259]. Zinc oxide nanoparticles have been widely utilised in scientific and practical research based on their non-toxic nature and ability to block the UV irradiation [259]. Zinc oxide nanoparticles can be applied to protect epoxy resins from environmental degradation and increase the toughness and antibacterial property [260].

Zabihi et al. showed that the addition 5% zinc oxide nanoparticle led to an impressive improvement of thermal and mechanical properties of DGEBA epoxy resin [253]. Mohan & Renjanadevi stated that the addition of 2% zinc oxide nanoparticle into the diglycidyl ether of bisphenol-A was improved the tensile strength by 50%, compared to that of pure DGEBA epoxy. They concluded that the excellent dispersion of 2% zinc oxide nanoparticle into epoxy resin produced significant improvements in the mechanical properties [261].

Titanium oxide nanoparticles were made to develop epoxy resins or polymers modified by nanofillers to improve the tribological performance of the epoxy matrix [262]. Chang et al. found that the addition of titanium oxide (TiO_2) nanoparticles to epoxy resin apparently reduced the frictional coefficient and significantly enhanced the wear resistance of the composites, particularly at high contact pressures and sliding velocities [263]. Xing and Li investigated the effect of silica particle size on the wear behaviour of epoxy nanocomposites at low levels of filler content and showed the smaller sized particles seemed to be more effective in improving the wear resistance [264]. Zhi et al. demonstrated that epoxy/TiO_2 nanocomposites, which the wear performance was better if the fillers were highly dispersed and homogeneous on the microscale significantly [265]. Another study showed that the addition of TiO_2 nanoparticles into epoxy resins improved could be homogeneously dispersed in epoxy by applying ultrasound, which improved the mechanical properties compared to epoxy without filler [266].

Several studies have found that Graphene oxide (GO) improved the toughness and enhanced the mechanical properties of epoxy resins [267]. Umer et al. investigated the improvement of GO/epoxy resins; they found out that 30% increase in flexural strength and 21% increase in flexural modulus are manifested by adding GO as the secondary reinforcement to glass fibre composites [268].

Wan et al. stated that the addition 0.25wt. % of graphene oxide nanoparticle (GO) into DGEBA epoxy resins improved the mechanical properties. They found that the tensile modulus and strength increased from 3.15 ± 0.11 to 3.56 ± 0.08 GPa (~13%) and 52.98 ± 5.82 to 92.94 ± 5.03 MPa (~75%), respectively after the incorporation of 0.25% GO into DGEBA epoxy, compared to that of the pure epoxy resin [269].

Currently, carbon nanotubes as fillers in an epoxy matrix have improved their acceptability for high-performance applications in terms of thermal, mechanical and electrical properties [270, 271]. Single-walled carbon nanotubes (SWCNTs) tend to agglomerate, which leads to heterogeneous dispersion in the epoxy composites [272,273]. The presence of various functional groups such as oxirane groups in the epoxy resin molecule increases its reactivity, and resin acquires new features that are non-typical of them before modification [274]. The addition of 1% carbon nanotubes to epoxy filled with timber gives a considerable improvement in mechanical properties, including a significant increase in tensile strength (43%) [275-277]. Figure 2.16 shows the interaction between epoxy resins and CNTs.

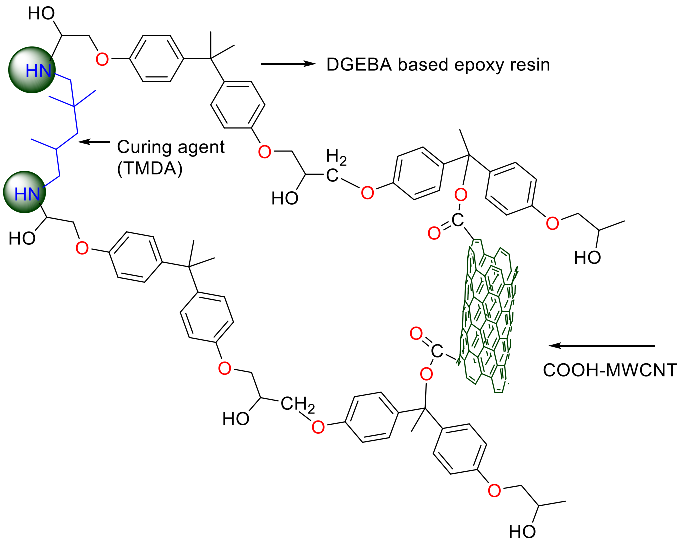


Figure 2.16: Interaction between cured DGEBA epoxy resin and CNTs

Alumina (Al_2O_3,) of 2% vol was found to improve mechanical of epoxy (flexural strength by 28%) [278]. The soft inorganic fillers such as graphite and molybdenum sulfide (MoS_2) are applied in the epoxy resins to make the epoxy composites more suitable for low friction and low wear environments [279]. Shi et al. [280] found that incorporation of nano-Al_2O_3 particles (4%) in the epoxy resin increased flexural modulus by 13% and flexural strength by 33% of the composite. Rodrigues and Broughton [281] noticed that the addition of 5% boron carbide in an epoxy composite increased the flexural and tensile strengths ranging between 24% and 56%.

The properties of epoxy resins have been improved by applying a wide variety of organic fillers [282,283]. Although there are some positive impacts of incorporating rubbers, the low glass transition temperature of the rubber filler can lower the maximum usable temperature and the modulus of epoxy adhesives [284-286]. On the other hand, high-performance thermoplastics such as polyetherimides, polyethersulfones, and polyketones have been used to enhance the chemical interaction of epoxy resins [287]. The thermoplastics have been applied as tougheners because they reduce the brittleness of the resins and thus minimise the compromise between toughness and thermal stability [288]. Polyurethanes have also been implemented to improve the toughness of epoxy resins. Polyurethane additives create grafts that interpenetrate with the epoxy resin network, which lead to significant improvements in the fracture toughness of the resins. Hydroxyl-terminated polybutadienes are also good candidates in improving the toughness of the epoxy resins, and for enhancing their flexibility [287,288,289].

2.14 Previous Studies on the Accelerated Weathering of Epoxy Resins

The current body of literature contains a significant number of studies on the impact of accelerated weathering on the properties of epoxy composites [290]. Chemical changes in an epoxy composite matrix resin were observed by Monney *et al*. [291,292] following UV irradiation with a xenon arc lamp. After accelerated weathering up to 1000 h, the samples exhibited a reduction in the infrared methyl and methylene peak intensities between 2800 cm^{-1} and 3000 cm^{-1}, the disappearance of aromatic ring peaks (1608 cm^{-1}, 1510 cm^{-1} and 1458 cm^{-1}) and the disappearance of C–O stretching peaks (1232 cm^{-1} and 1045cm^{-1}).

Kumar *et al*. [30] found that cyclic exposure to UV radiation and condensation for a carbon fibre-reinforced epoxy composite caused severe erosion of the epoxy composite, resulting in a 29% reduction in tensile strength after exposure for 1000 h.

Segovia *et al*. [293] observed that the glass fibre/epoxy composites exposed to 7000 h of UV irradiation, the elastic modulus and tensile strength was reduced by 15% and 20%, respectively. Elongation at the break increased from 20% to 56%. Most of the degradation was observed primarily in the surface of the epoxy resin; the interior of the glass fibre/epoxy composite appeared to remain intact.

Pang *et al*. [294] reported on glass/epoxy composites that were exposed to artificial UV exposure for 48 h. No visual changes were recorded in the samples, but the deflection at maximum load increased by 20%. Scanning electron microscopy (SEM) analysis showed delamination, interfacial debonding, and cracking in the weathered samples. It was concluded that UV exposure significantly decreased the toughness and cracking resistance of the glass/epoxy composites.

Phelps and Long [295] exposed unidirectional graphite/epoxy coupons to UV radiation in a solar simulator for four weeks, after which the flexural strength of the samples was tested. No significant changes were observed in the flexural samples after exposure in comparison to the unexposed controls.

Larsson [296] conducted a study on the effect of UV exposure on the mechanical properties of fibre-DGEBA epoxy composites; the results showed losses in the tensile strength (23% loss after 1000 h and 43% loss after 2000 h). No changes in tensile modulus were recorded for any of the samples, regardless of the exposure time.

Tonozuka et al. [297] investigated the effect of simulated weathering at 175 ℃ for 1000 h using an oven in the atmosphere on the mechanical properties of bisphenol type F epoxy-copper composites. They reported that the tensile strength of the epoxy resin was 83 MPa before aging; after exposure for 1000 h, it decreased to 41 MPa. They noticed that the tensile strength of the copper joint with epoxy resin had a lower reduction than that of the epoxy resin without copper after 1000 h of aging [297].

Singh et al. [228] found that alternating three hours cycles of UV radiation and water vapour condensation at 50 ℃ degraded the flexural strength of epoxy up to 81% and induced the removal of the surface layers of EPON 862 (DGEBA epoxy). Exposure to a constant relative humidity of 80% at 50 ℃ resulted in a 47% reduction in the flexural strength; however, interestingly, it increased the flexural modulus, while the cyclic exposure decreased the modulus [228].

Rezig et al. [298] reported a loss in the thickness and an increase in the surface roughness of epoxy resin after exposure to UV at 50 ℃, with higher degradation occurring at higher relative humidity.

Hu et al. [299] found that cyclic exposure of epoxy-coated steel plates to radiation and condensation resulted in a decrease in the resistance of the epoxy coating after 28 days.

Moreover, the adhesion strength between the epoxy and the steel plates was reduced by more than 50% with exposure.

Silva and Biscaia [300] also found little to no loss in the tensile strength properties for samples exposed to various environments. They tested commercial glass fibre reinforced plastic (GFRP) composites that were exposed to salt, fog, humidity cycles and UV degradation. No change in tensile modulus was found for water immersion at room temperature and UV exposure, and a difference of less than 10% loss was observed for the temperature and salt fog cycles. No change was found in the tensile strength under room temperature water, and a less than 12% loss was found for all other conditions after 10,000 h of exposure [300].

Comparing with all the previous works mentioned above that are due to the effect of the environmental conditions on the heat-cured epoxy, some studies have investigated the impact of the environmental conditions on the mechanical and thermal properties of cold-cured epoxy resins. For instance, Maljaee et al. (2017) were investigated addressing the effect of environmental conditions on thermal properties of a cold-curing epoxy resin (DGEBA) [301].

Another study was reported that modified cold cured epoxy composites (Organic-inorganic hybrid resins) were improved the thermal resistance. They concluded that the cold-curing system improved the thermal and mechanical properties of the epoxy composites [302].

As seen in the previous studies mentioned above, very few researchers have investigated the impacts of accelerated weathering on aromatic epoxy resins and aliphatic epoxy resins with one type of fillers using combined degradation conditions. A few researchers only examined the effects of UV irradiation of DGEBA epoxy (aromatic epoxy) filled with an inorganic filler (carbon fibre) and assessed the mechanical degradation for short-term exposure conditions. Some researchers evaluated the impact of accelerated weathering (combined conditions) and evaluated the changes using the FTIR technique. By comparing the present study with previous work mentioned above, this research was developed to cover all possible factors that could resist the degradation for more extended periods as a result of the effects of combined accelerated weathering conditions. The current research study applied two epoxy resin from the same class, DGEBA (aromatic structure) and HDGEBA (aliphatic structure). Unlike DGEBA epoxy, HEGEBA (aliphatic epoxy) has never been used to evaluate accelerated weathering.

In comparison to previous work, the current study used various additives as stabilisers that were incorporated into two epoxy resins. The changes were evaluated by using several measurements, such as FTIR, SEM, XRD, mechanical tests and thermal measurements (TGA and DSC). In comparison to DGEBA, HDGEBA incorporated into different fillers demonstrated a significant ability to inhibit the degradation for a longer period of exposure.

Chapter 3: Materials and Methods

3.1 Experimental Design and Result Analysis

The experiments were designed to examine the effects of different weathering times on the chemical, thermal and mechanical properties of two cured epoxy resin (Diglycidyl ether of bisphenol A, DGEBA and the hydrogenated diglycidyl ether of bisphenol A, HDGEBA) and their composites. Three photostabilisers were selected as additives of two cured epoxy resins: Multi-walled carbon nanotubes (MWCNT), calcium sulfate particles (CS) and microcrystalline cellulose (MCC). All samples were exposed to various environmental (UV irradiation and moisture) conditions with different accelerated weathering cycle times (1, 2, 3, 4, and six months). Several properties such as surface chemistry (Fourier Transform Infrared, FTIR), thermal properties (thermal gravimetric analysis, TGA and differential scanning calorimetry, DSC), mechanical properties (tensile tests), morphology tests (scanning electron microscopy, SEM), and the structural changes (XRD analysis) were tested to evaluate the impacts of artificial weathering on the epoxy resins and epoxy composites.

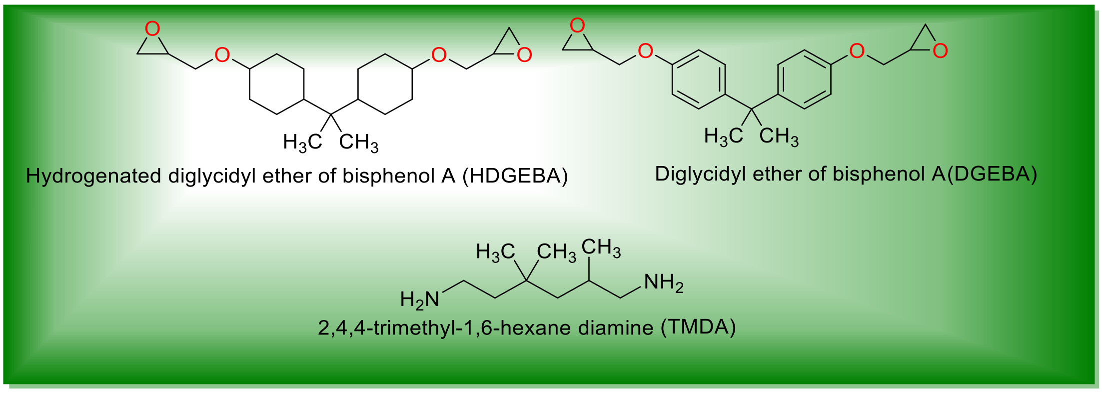
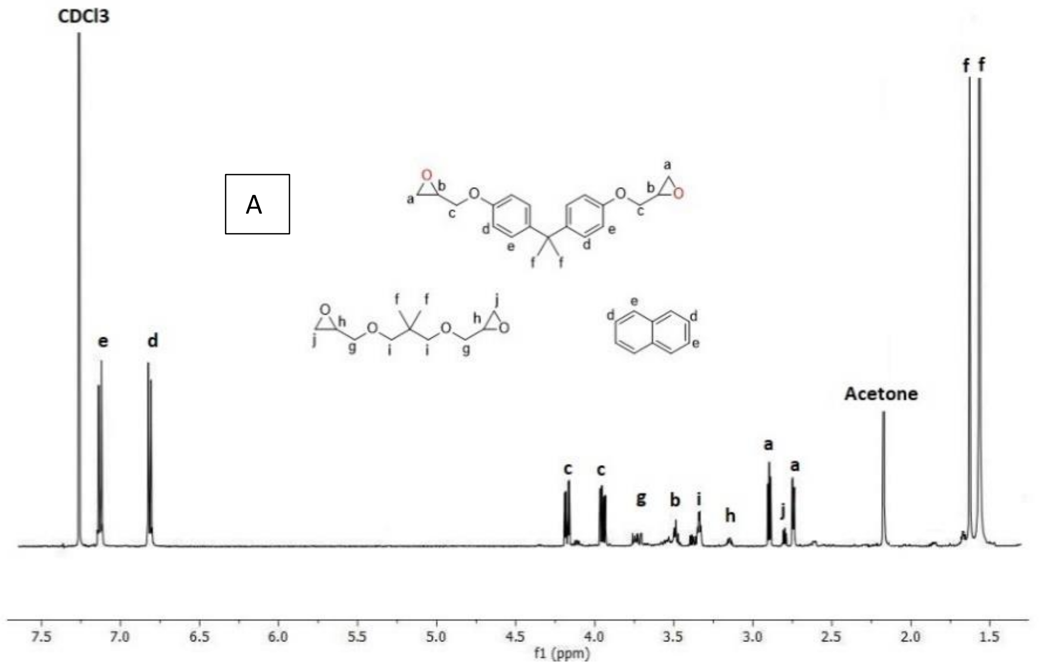


Figure 3.1. Chemical structures of the epoxy resins and curing agent.

3.2 Materials

3.2.1 Epoxy Resins

The epoxy resin Sikadur 330A were provided by Sika Pty. Ltd., Australia, which contain diglycidyl ether of bisphenol A (DGEBA) with hydrocarbon solvent (naphtha compound) and Epalloy 5000 (the hydrogenated diglycidyl ether of bisphenol A, HDGEBA) was provided by (Brentage Australia Ltd.). The curing agent (Sikadur 330B) is expressed by the chemical structure (2, 2, 4-trimethyl-1, 6-hexadiamine) was provided by (Sika Pty. Ltd.), Australia. The ratios of epoxy resins and curing agent (100:40 wt./wt.%) was used in this work. The chemical compositions of the industrial epoxy resins and curing agent were identified by utilising NMR and GC-MS spectrometers. Figures 3.2 shows ^{1}H-NMR spectra of the industrial epoxies and curing agent.



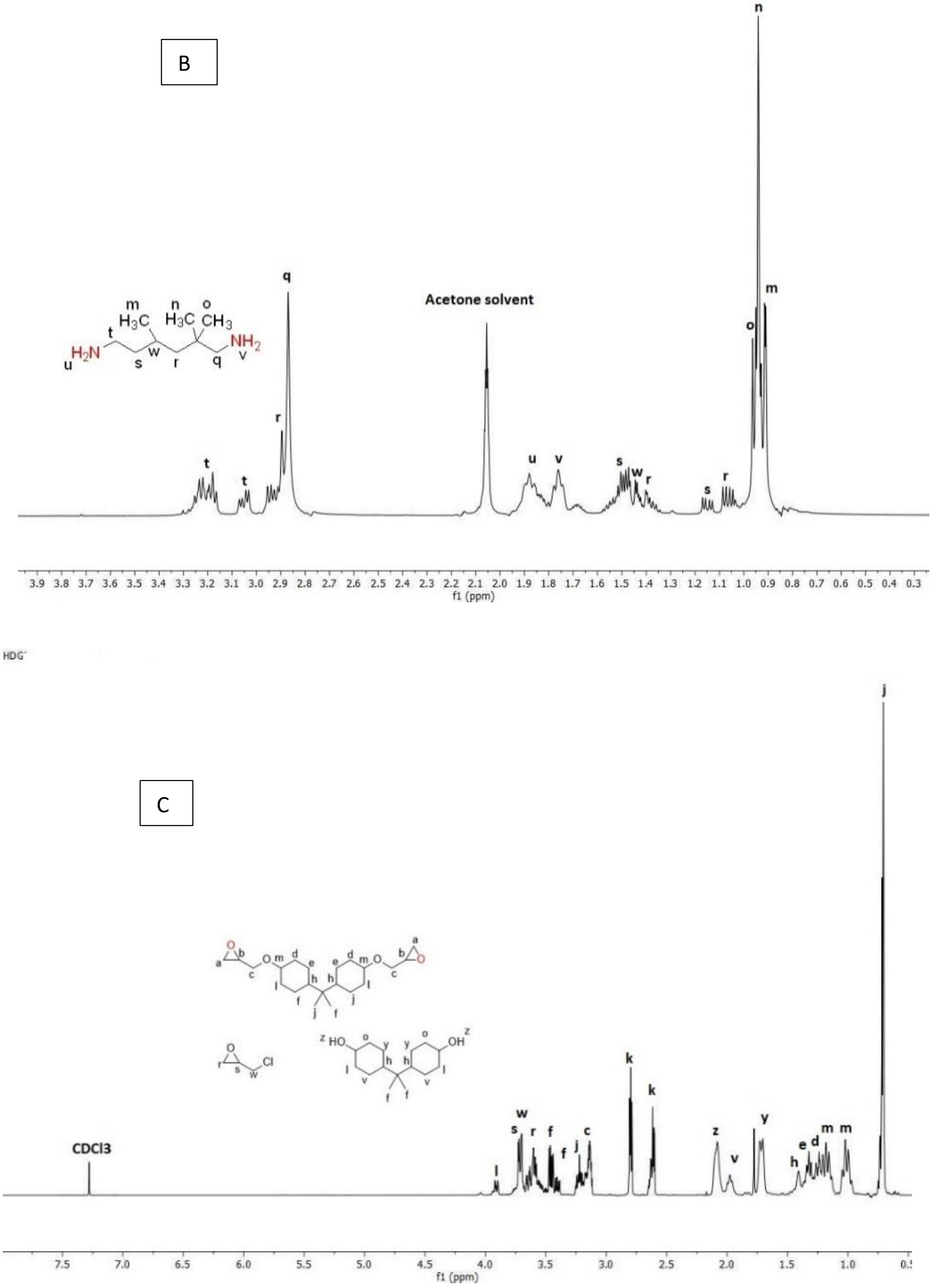


Figure 3.2: ¹H-NMR of Sikadur 330A (A), Sikadur 330B (B), and Epalloy 5000 (C)

3.2.2 Oxidised MWCNT Preparation

Pristine MWCNT (ANT Applied Nano Technologies, Australia) was blended with a mixture of 3:1 ratio of concentrated sulfuric acid (H_2SO_4, 98%) and nitric acid (HNO_3, 70%) and then sonicated for 4 hours at 40 °C in an ultrasonic bath to produce carboxylic acid groups on the surface of MWCNT [270]. After sonication the mixture was added dropwise to cold distilled water, oxidised MWCNT were filtered and dried in a vacuum oven (type Thermolineat, Model: LVO-70, NSW, Australia) at 80 °C for five hours [303]. The scheme in Figure 3.3 shows the preparation of functionalised COOH-MWCNT and then is identified by FTIR spectra, as shown in Figure 3.4, where are appearing at the carboxylate peak on the modified MWCNT spectra. The purpose of this procedure is the functionalisation of the MWCNT surface can enhance linkage with the epoxy to enable a stress transfer between the epoxy and the MWCNT filler. The addition of carboxylic acid groups on the MWCNT surface enabled better dispersion with epoxy resins [304].

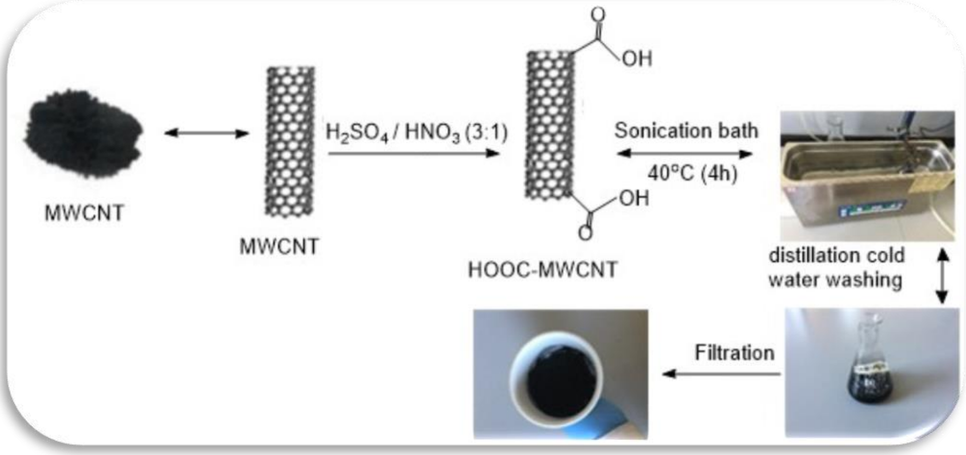


Figure 3.3: Scheme for the synthesis of carboxylated functionalised MWCNT

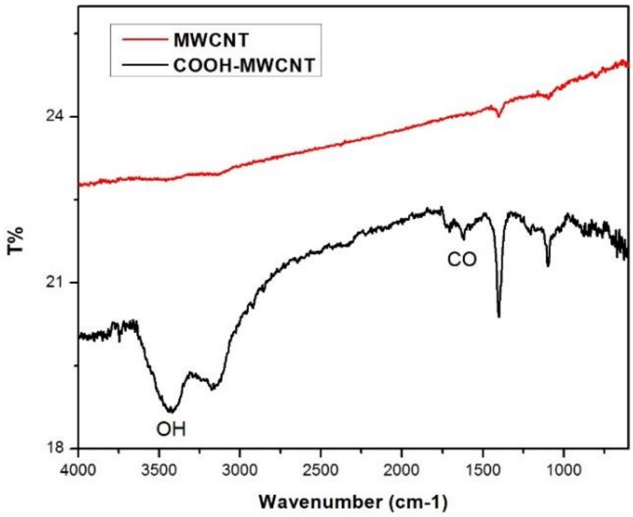
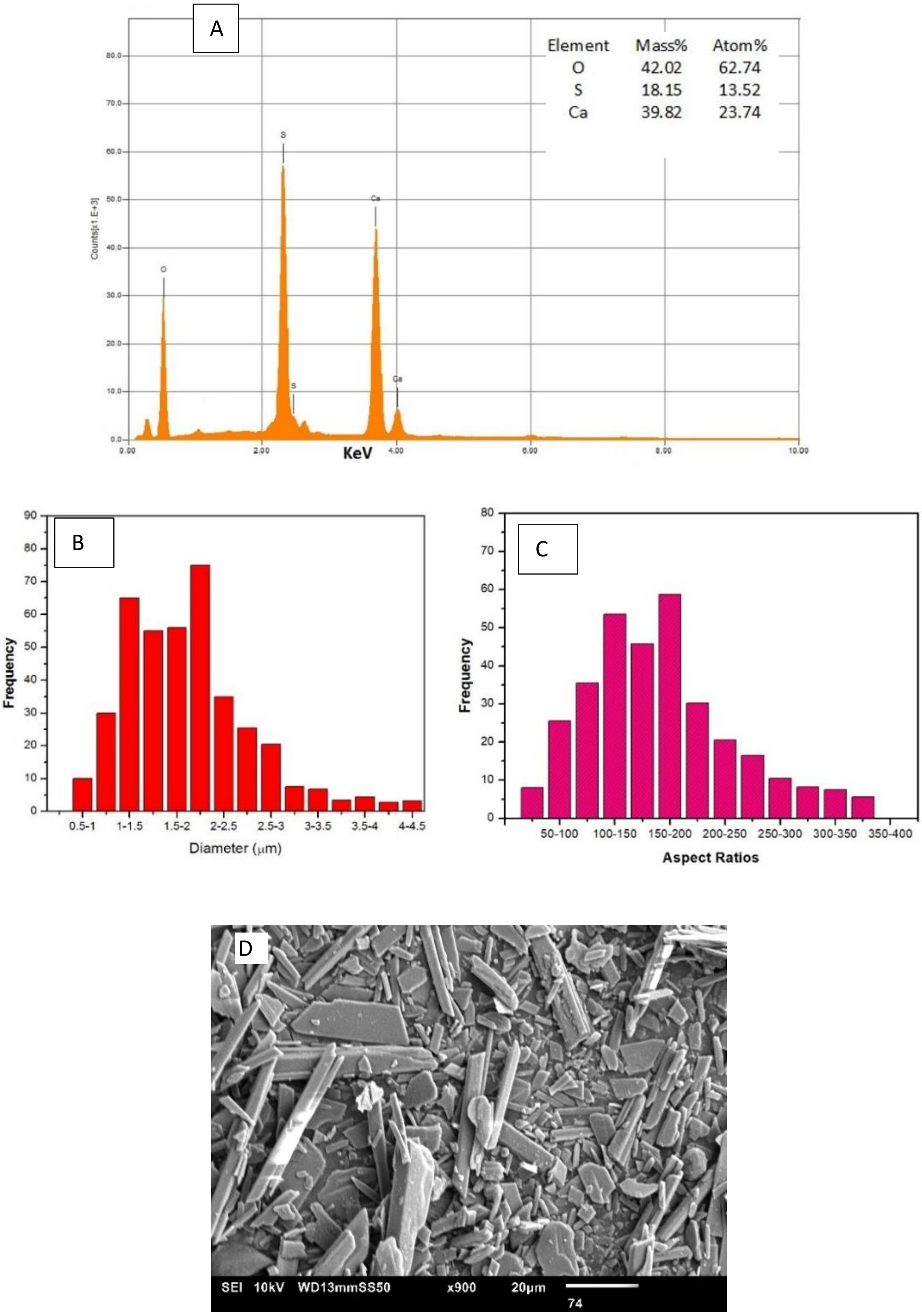


Figure 3.4: FTIR spectra of MWCNT and COOH-MWCNT

3.2.3 Calcium Sulfate Preparation

Calcium chloride ($CaCl_2$. $2H_2O$) and sodium sulfate (Na_2SO_4) were supplied by Sigma-Aldrich, Sydney, NSW, Australia.

Calcium sulfate dihydrate was prepared by a dropwise addition of 250 mL of 0.5M sodium sulfate solution in de-ionised water was added to a 250 mL solution of 0.5M calcium chloride solution. The two solutions were mixed and with continuous magnetic stirring at 70 °C over a period of 2 hours until the white precipitate of the insoluble salt is formed [304]. The precipitate was filtered off by using a filtration paper and the filtered precipitate was washed several times with deionised water until salt-free. The filtered calcium sulfate salts dried in a vacuum oven at 120 °C for four hours [305] and calcium sulfate particles were identified by FT-IR spectrometer, energy-dispersive X-ray spectrum (EDS) and crystals of CS were determined by SEM (Figure 3.5).



Element	Mass%	Atom%
O	42.02	62.74
S	18.15	13.52
Ca	39.82	23.74

Figure 3.5: EDS spectrum (A), particle size distribution (B), aspect ratios (C), and SEM micrograph (D) of CS ($CaSO_4$) particles

3.2.4 Cellulose Microcrystalline (MCC)

Microcrystalline Cellulose (MCC) with particle size 10µm was supplied from Asahi Industry Chemical Co. Ltd. (Japan). Figure 3.6 illustrates the SEM micrograph and the size distribution of MCC filler.

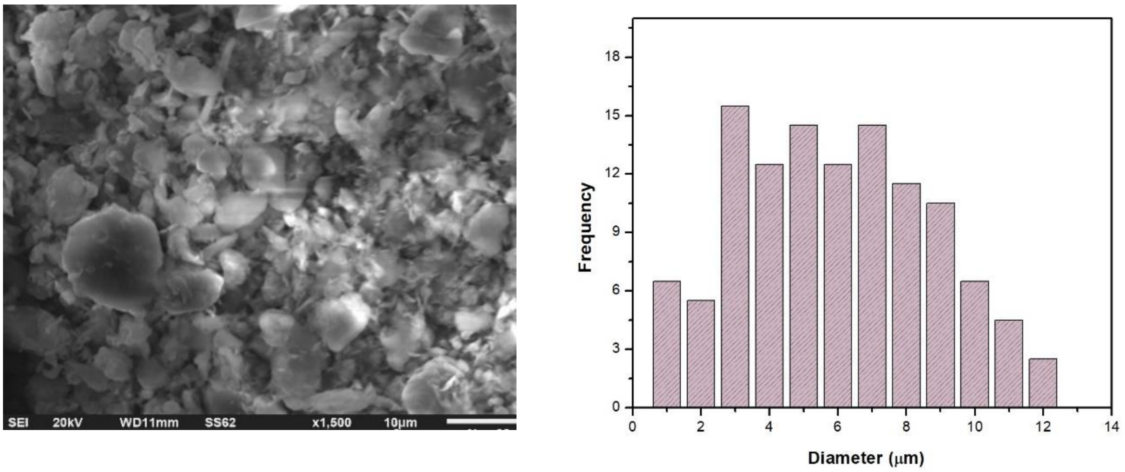


Figure 3.6: SEM micrograph (A) and size distribution (B) of MCC filler

3.2.4 GC/MS and NMR Analysis of uncured epoxy resins

Five grams of epoxy resin composite materials were extracted with 250 mL acetone (Sigma-Aldrich, NSW, Australia) for overnight on a Soxhlet apparatus and then concentrated on a rotary evaporator. The samples were analysed by using GC-MS type (Agilent Technologies 7890 A GC System, USA). For each test, around 1µg of samples were dissolved with 5 ml acetone, using GC/MS vial tubes. The stationary phase of the GC column was polysiloxane (UA-1 model, Frontier Lab Ltd., Japan). The GC temperature was initially started at 50 ºC and then ramped to 250 ºC at 20 ºC·min^{-1} with a soak time of 20 minutes. The data were searched for matching compounds using the NIST MS library.

To confirm the chemical structure of the commercial epoxy resins and curing agent, which were used in this work, The concentrated epoxy resins and curing agent products of samples were analysed using nuclear magnetic resonance (^{1}H-NMR) measurement and conducted on

(Bruker^{TM} 500 ASCEnd spectrometer, Germany). The deuterated solvent to dissolve the commercial epoxy samples was chosen in each case is the most common ones (chloroform-d, $CDCl_3$). The experimental conditions in the case of ^{1}H-NMR tests were 500 MHz of the magnetic field.

3.3 Cured Epoxy Resins Preparation

A fixed amount of epoxy resin DGEBA (Sikadur330A) or HDGEBA (Epalloy 5000) was mixed with a curing agent, TMDA (Sikadur 330B) in the ratio 4:1 by weight and mixed with gentle stirring to minimise air bubbles. Then, the mixture of epoxy resins were poured into PTFE dog-bone shaped moulds with a dimension (50 mm length, 20 mm width, and 2 mm thickness) according to the standard (ISO 527), as shown in Figure 3.8. The epoxy mixtures were allowed to cure in a vacuum oven at 50 ℃ for 5 hours for cured DGEBA epoxy and 10 hours for cured HDGEBA epoxy. After that, the specimens were removed from the moulds and kept in an airtight container for further experimentation. Figure 3.6 displays the curing mechanism reaction of epoxy resin and Figure 3.7 shows the PTFE (A), and dog-bone shape to make up the epoxy resin samples.

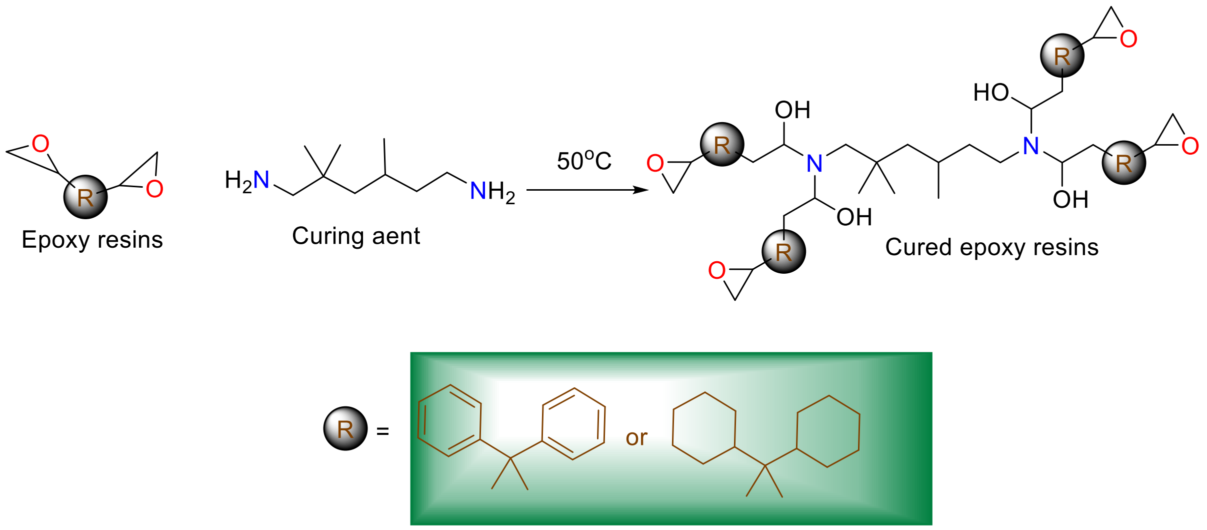


Figure 3.7: The reaction mechanism of cured epoxy resins

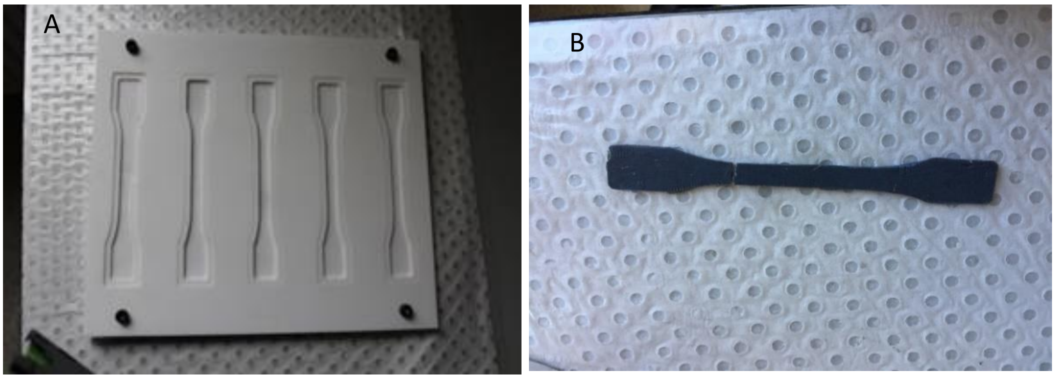


Figure 3.8: (A) PTFE mould used in this work and dog-bone shape (B) for cured epoxy resin

3.4 Preparation of Epoxy Resins/Fillers Composites

DGEBA and HDGEBA epoxy resins were blended with 0.5 wt.% acid treated MWCNT, 2 wt.% CS, and 2 wt.% MCC fillers and stirred for 10 minutes at room temperature to allow in removing the air bubble from the mixture.

Epoxy resins/acid treated MWCNT mixture was poured into a PTFE mould to provide a dog-bone shape with the dimensions of 50 mm length, 20 mm width, and 2 mm thickness according to the standard (ISO 527). Later, the samples were cured in a vacuum oven at 50 °C for 5 hours of DGEBA and 10 hours of HDGEBA composites [306]. All samples were cured at ambient conditions (25 °C for seven days) before exposing to accelerated weathering conditions.

Table 3.1: Formulations in preparation of the compositions of epoxy resins and epoxy composites

DGEBA (wt.%)	HDGEBA (wt.%)	TMDA (wt.%)	MWCNT (wt.%)	MCC (wt.%)	CS (wt.%)
40	40	10	-	-	-
38	38	10	-	2	2
39.5	39.5	10	0.5	-	-

3.5 Testing Methodology

3.5.1 Accelerated Weathering Test

Epoxy resins and epoxy composites were subjected and exposed to UV radiation, using a chamber manufactured in-house by Brien Holden Ltd. NSW, Australia, equipped by UV lamps producing a collimated and highly uniform UV flux of approximately $140\mathrm{W \cdot m^{-2}}$ in the UVA (295 nm to 400 nm) range, which is the most detrimental range for epoxy resin degradation. The specimens were exposed to UV irradiation for one week, then inverted and exposed for a further week [306].

3.5.2 Moisture Tests

The weathered samples were exposed to 100% relative humidity at an elevated temperature approximately 50±5°C [189] for two weeks, using a moisture curing tank type (Tinius Olsen, Model: P0-335-4-03, USA). The experiments were carried out at 50 °C to raise the rate of degradation [189,307]. This procedure was then repeated, to provide total accelerated weathering times of 4, 8, 12, 16 and 24 weeks for each set of samples; throughout the text, these times will be approximated to 1, 2, 3, 4 and six months [306]. Figure 3.9 displays moisture and UV chambers, which were utilised for accelerated weathering tests.

Figure 3.9: Moisture tank (A) and UV-irradiation chamber (B) used for accelerated weathering tests

3.5.3 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transformed infrared spectroscopy (FTIR) is a convenient technique and is widely utilised to characterise polymer and polymer nanocomposites. It is one of the most powerful analytical techniques used of determining the chemical groups in a molecular structure and of identifying the number of components in the system.

The ATR-FTIR spectra of all samples were recorded by utilising (ATR-FTIR, Perkin Elmer Spectrometer Type Two with diamond/ZnSe ATR, Model L1600300, Llantrisant, UK), as shown in Figure 3.10. All samples were dried in a vacuum oven at 40°C for 2 hours before the measurement. The FTIR spectra were tested within the range of 700-4000 cm^{-1} because the significant changes in the interest functional groups were within these areas [308]. The carbonyl and hydroxyl indices were calculated based on the Equations 3.1 and 3.2 [308], they applied to analyse the oxidation degree of epoxy resins and epoxy composites before and during the exposure to different exposure times of accelerated weathering, which is the I_{abs} represents the intensity of absorption [308]:

$$\text{Carbonyl index} = \frac{I_{abs}\text{at 1654 cm}^{-1}}{I_{abs}\text{at 2877 cm}^{-1}} \times 100\% \qquad (3.1)$$

$$\text{Hydroxyl index} = \frac{I_{abs}\text{at 3300 cm}^{-1}}{I_{abs}\text{at 2877 cm}^{-1}} \times 100\% \qquad (3.2)$$

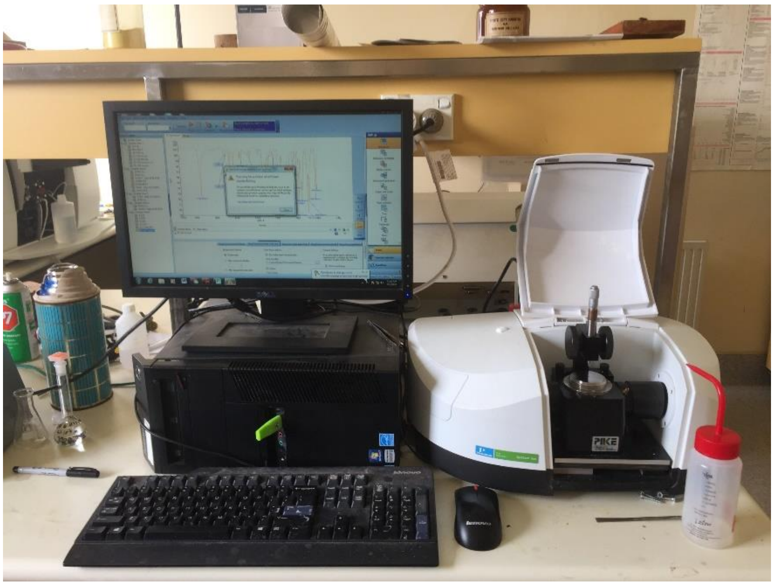


Figure 3.10: Perkin Elmer FTIR Spectrometer type two

3.5.5 Tensile Strength Tests

Tensile strength was measured by using a universal testing machine (UTM, Industrial Series DX 300KN, Instron Ltd., Bayswater, Australia). The specimens were tested according to the standard ASTM-D 638, using the dog-bone shape with dimensions 50 mm length, 20 mm width, and 2.5 mm thickness. The testing speed was 10 mm·min^{-1}. All specimens were dried at an oven at a temperature of 50 °C of 2 hours prior testing to make sure that all samples were treated to remove any residual moisture.

All samples placed vertically between the grips of testing machine and tensile stress-strain curves plotted during the test [306]. Five replicates of each sample were tested for each set of conditions. Figures 3.11 and 3. 12 show the test set-up of weathered epoxy resin sample under the tensile tests machine and stress-strain curve was obtained from the tensile test software program.

Figure 3.11: Universal Instron machine for tensile tests set-up

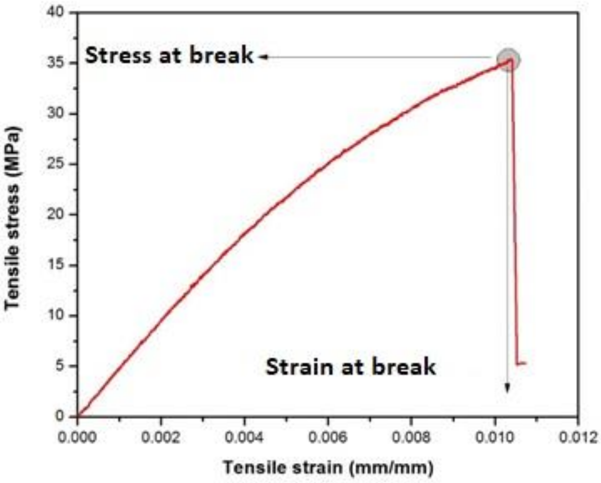


Figure 3.12: Stress-strain curve of cured DGEBA epoxy resins before exposure

3.5.6 TGA Analysis

Thermogravimetric analysis (TGA) was selected to study the thermal degradation of epoxy resins and their composites, and also to determine the mass changes, in relation to temperature. All samples were assessed of thermal tests before and after exposure, utilising the thermogravimetric instrument type (TA Instruments Hi-Res TGA 2950), as shown in Figure 3.13. To test the performance of TGA was calibrated with (calcium oxalate, providing from Sigma-Aldrich, USA) as a standard. The weights of samples were approximately within the range of 5-10 mg and they were placed in an aluminium pan, and then heated from 30-500 °C at a heating rate of 10 °C·min^{-1}. TGA and DTG curves were obtained from the instrument runs and were utilised to determine the percentage of mass loss and the decomposition temperatures with the number of degradation steps, respectively. The percentage of residues left after the TGA runs represent the materials' residual yield.

Figure 3.13: Thermogravimetric analysis (TGA) instrument

3.5.7 DSC Analysis

A differential scanning calorimeter (DSC) was utilised to determine the decomposition temperature and the glass transition temperature (T_g) of all samples before and after the exposure for different accelerated weathering times. DSC was carried out utilising a Perkin-Elmer differential scanning calorimeter, as shown in Figure 3.14 (A) under a nitrogen atmosphere. The methodology was as follows: Approximately, small samples (2 mg) were tested under conditions with heating rates of 2 °C·min^{-1} from 30 °C to 250 °C. The values of glass transition temperature, T_g, for the epoxy resin and epoxy composites were obtained from the plot of heat flow against temperature curves [309]. The T_g values were determined based on the inflection point of endothermic DSC curves, as shown in Figure 3.14(B). DSC curves were utilised to detect the possible post-curing and physical aging impacts of epoxy and epoxy composites [309].

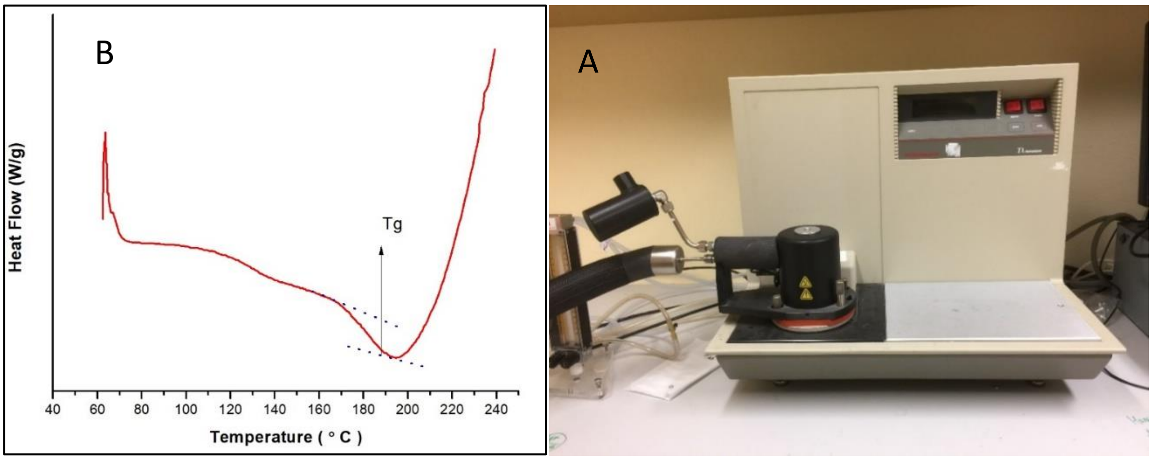


Figure 3.14: Differential scanning calorimetry (DSC) instrument (A) and the inflection point of endothermic DSC curve (B)

3.5.8 DMA Analysis

Dynamic Mechanical Analysis (DMA) is non-destructive testing performed to obtain material’s mechanical properties. Storage modulus, loss modulus and the loss factor are some of the mechanical properties the DMA can test for. When a sample is tested with the DMA, two sets of data were recorded (the loss factor and storage modulus). The force and displacement applied were recorded from the material deformation.

The dynamic mechanical analysis was carried out at the Australian National Fabrication Facility (ANFF) at the University of Queensland, using a Mettler Toledo DMA/SDTA861 (Figure 3.15). The equipment was operated in a dual cantilever mode (oscillation amplitude: 15 µm): a heating rate of 5 °C·min^{-1} in the air and a frequency of 1 Hz. Also, the analysis was carried out from room temperature to 270 °C. DMA rectangular samples were prepared with dimensions of 40 mm length, 10 mm width, and 2.5 mm in thickness. The data, which includes storage modulus and tan δ, were recorded by the TA Instrument explorer software and were plotted against temperature.

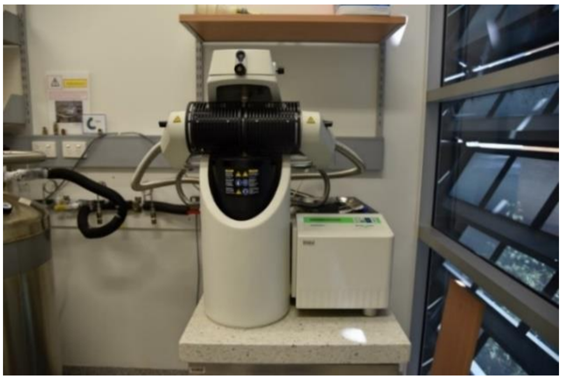


Figure 3.15: Dynamic mechanical analysis (DMA) instrument

3.5.9 XRD Analysis

The X-ray scattering intensity of additives, epoxy resins and epoxy composites before and after exposure were investigated. X-ray diffraction was carried out by using a PANalytical Aeris, UK (Figure 3.16), applying CuKα (λ = 1.54 Å) radiation. A diffraction intensity was measured over the range of 5-80° (2θ range), operated at a voltage of 40 kV and a current of 15 mA. X-rays were collimated from two pinholes and were incident generally on the sample and pressed between two mylar sheets. The patterns were recorded on a flat film and kept at a distance of 2.5 cm from the sample.

Figure 3.16: X-ray diffraction (XRD) instrument

3.5.10 SEM Analysis

All samples were cut down to be utilised to SEM photograph applying a Scanning Electron Microscope (SEM). The dimensions of samples were cut to roughly 8 mm x 2 mm x 2 mm. The samples were cleaned off with acetone. The SEM samples were dried at 50 °C for two h by utilising a vacuum oven.

The surface morphology of all samples (epoxy resins and epoxy composites) before and after exposure to different accelerated weathering was evaluated, utilising A JEOL 6020 Scanning Electron Microscope (JEOL Pty. Ltd. USA), as shown in Figure 3.17. The SEM micrographs were utilised to investigate the changes on the surface of all samples before and after exposure to different accelerated weathering periods. The samples prepared were coated by applying a gold coating, using an MP-19020NCTR Neocoater before visualisation.

Figure 3.17: Scanning Electron Microscopy (SEM) instrument

CHAPTER 4: Chemical Degradation (FTIR)

Reflectance infrared spectroscopy is developed progressively as an appropriate method of investigating organic polymers or epoxies on the surface. The chemical changes on the epoxy and epoxy composites were analysed to investigate the depth profile of the degradation [310]. ATR-FTIR is a common instrument to follow the UV degradation process, which allows to assess different degradation products and to define the degradation index of a polymer or an epoxy with more details [311].

In the transmission technique of IR sampling is Attenuated Total Reflectance (ATR). In place of the IR beam passing through the sample, the beam is shifted through an ATR crystal which is in connection with the sample. The beam represents an evanescent wave that extends into the sample, only when the crystal has a higher refractive index than the sample measured. The intensity of the evanescent wave declines exponentially with distance from the interface. The penetration depth (*PD*) into the sample is typically 0.5 to 2µm, or close to the surface, but depends on many factors, as shown in equation 4-1 [312].

$$PD = \frac{\lambda}{2\pi\, n\, IRE\sqrt{\sin\theta - (\frac{nS}{nIRE})^2}} \tag{4-1}$$

Where λ is the wavelength of the incident light, nIRE is the refractive index of the crystal, and *nS* is the refractive index of the sample, θ is the angle of incidence.

4.1 Chemical Degradation of DGEBA and DGEBA Composites by FTIR

FTIR analysis was performed to monitor the changes in the chemical compositions of epoxy composites (DGEBA and DGEBA/0.5% MWCNT, DGEBA/2% MCC and DGEBA/2% CS) before and after exposure to different accelerated weathering times. Previous studies have shown that carbonyl and hydroxyl groups are generated by degradative oxidation reactions, following the chain scission and hydrogen abstraction from the polymer backbone [313]. The area between 1600 cm^{-1} and 1800 cm^{-1} (area 1=1654 cm^{-1}) is due to the carbonyl index while the area between 3200 cm^{-1} and 3700 cm^{-1} (area 2=3300 cm^{-1}) is corresponding to hydroxyl groups as shown in Figure 4.1. FTIR spectra were measured the surface of samples before and after exposure to different durations of accelerated weathering, detected an increasing relative intensity of a hydroxyl group band at 3300 cm^{-1} and a carbonyl group band at 1654 cm^{-1} (Figures 4.1-4.4). These were assessed quantitatively by comparison of peak heights with the height of the band in the C-H stretching region at about 2900 cm^{-1}. Aromatic C=C stretching can also contribute to the spectra in the 1500-1700 cm^{-1} range while residual NH_2 from unreacted crosslinker may be apparent in the 3300 cm^{-1} area [313], so the indices which were reported in equations 2.1 and 2.2 [308], are not zero before accelerated weathering; it is the change in these values with time which is significant for assessing performance.

For DGEBA epoxy, there is an initial reduction in the C-H stretching region at about 2900 cm^{-1}, after which little change occurs in this region. The carbonyl index of unexposed DGEBA epoxy specimen (47±3%) was much higher than for DGEBA/0.5% MWCNT (34.5±5.7%), DGEBA/2% CS (32.5±3%) and DGEBA/2% MCC (40±3.6%) composites (Figure 4.5 and Table 4.1).

Table 4.1: The carbonyl indices of DGEBA, DGEBA composites and HDGEBA, HDGEBA composites before and after exposure to different accelerated weathering times.

Samples	Exposure times	Carbonyl index (*I*co, %)	Samples	Exposure times	Carbonyl index (*I*co, %)
DGEBA	Control	47.2±3.1	HDGEBA	Control	34.5±5.7
-	1 month	81.4±4.3	-	1 month	38.7±8.2
-	2 months	86.2±4.8	-	2 months	45.8±7.6
-	3 months	87.5±5.7	-	3 months	57.5±9.3
-	4 months	152±3.5	-	4 months	62.7±8.7
-	6 months	184.4±12.4	-	6 months	70.1±12.9
DGEBA /0.5% MWCNT	Control	34.5±5.7	HDGEBA /0.5% MWCNT	Control	20.5±2.6
-	1 month	38.7±8.2	-	1 month	28.5±4.2
-	2 months	45.8±7.6	-	2 months	33.8±5.8
-	3 months	57.5±9.3	-	3 months	42.2±6.5
-	4 months	62.7±8.7	-	4 months	45.1±7.8
-	6 months	70.1±12.9	-	6 months	50.4±9.1
DGEBA /2% CS	Control	32.5±2.5	HDGEBA /2% CS	Control	22.4±2.8
-	1 month	34.3±2.7	-	1 month	25.6±3.2
-	2 months	39.8±2.4	-	2 months	32.8±3.8
-	3 months	55.2±3.7	-	3 months	40.8±4.2
-	4 months	68.7±4.3	-	4 months	45.5±5.2
-	6 months	82.7±2.9	-	6 months	53.7±6.2
DGEBA /2% MCC	Control	40.2±3.6	HDGEBA /2% MCC	Control	30.7±3.4
-	1 month	43.7±5.6	-	1 month	29.8±2.7
-	2 months	58.4±6.8	-	2 months	26.6±2.4
-	3 months	63.9±5.9	-	3 months	35.8±3.9
-	4 months	77.6±7.3	-	4 months	42.7±4.2
-	6 months	89.9±7.9	-	6 months	55.9±4.6

After six months' exposure, the carbonyl indices of DGEBA/0.5% MWCNT, DGEBA/2% CS, and DGEBA/2% MCC were approximately 70.1±12.9%, 82.7±2.9%, and 40.2±3.6%, and they displayed fewer increases than that of DGEBA epoxy. After six months of exposure, the increases in the carbonyl indices of DGEBA/0.5% MWCNT, DGEBA/2% CS, and DGEBA/2% MCC reduced to around 62%, 55%, and 51%, respectively, in comparison to that of DGEBA epoxy. There were slight changes in the carbonyl indices after exposure to one, two, and three months of DGEBA/0.5% MWCNT (38.7±8.2%; 45.8±7.6, and 57.5±9.3%), DGEBA/2% CS (34.3±2.7%, 39.8±2.4%, and 55.2±3.7%), and DGEBA/2% MCC (43.7±5.6%, 58.4±6.8%, and 63.9±5.9%) composites compared to those of the carbonyl indices of DGEBA epoxy samples (81.4±4.3%, 86.2±4.8%, and 87.5±5.7%) at the same times. In comparison with this study, previous work was reported on DGEBA-based resin filled with 4% oil fly ash (OFA) under a six months regime of accelerated weathering with moisture and UV. They noticed that over six months of exposure to accelerated weathering (UV and humidity) of DGEBA resin-filled 4% OFA, the carbonyl index rose from 90 to 440 % in the absence of OFA filler and only from 100 to 130% in the presence of OFA filler [314]. However, this experiment showed a very high level of degradation in the control sample (carbonyl index of 440%) and the results obtained here could be compared favourably with the absolute value of increasing the carbonyl index for the OFA filled sample (40%). The MWCNT filler in epoxy resins improved the interfacial strength of the epoxy matrix and the MWCNT aggregated and formed a high density, entangled network structure which reduced the degradation of epoxy composites after six months accelerated weathering because MWCNT formed a network on the surface of the epoxy samples [315]. Another work reported the degradation of an epoxy/CNT composite under intensive UV-light and investigated the mass loss of epoxy and epoxy composites by using thermal analysis. The results indicated that the epoxy composite (DGEBA/CNT) degrades slower than the neat epoxy (DGEBA) [313].

Table 4.2: The hydroxyl indices of (DGEBA, DGEBA composites) and (HDGEBA, HDGEBA composites) before and after exposure to different accelerated weathering times

Samples	Exposure times	Hydroxyl index (I_{OH}, %)	Samples	Exposure times	Hydroxyl index (I_{OH}, %)
DGEBA	Control	30.6±3.4	HDGEBA	Control	22.4±2.7
-	1 month	37.9±2.3	-	1 month	25.6±3.2
-	2 months	47.7±2.6	-	2 months	32.8±3.7
-	3 months	54.7±4.8	-	3 months	45.8±4.2
-	4 months	70.9±6.2	-	4 months	54.7±5.4
-	6 months	135.9±8.1	-	6 months	58.9±6.5
DGEBA /0.5% MWCNT	Control	19.8±1.7	HDGEBA/0.5% MWCNT	Control	20.7±1.2
-	1 month	24.8±2.4	-	1 month	17.6±1.8
-	2 months	33.6±2.1	-	2 months	18.9±0.9
-	3 months	38.7±2.6	-	3 months	20.1±1.4
-	4 months	46.8±3.8	-	4 months	25.9±2.1
-	6 months	67.8±3.8	-	6 months	31.1±2.7
DGEBA/2% CS	Control	20.5±2.7	HDGEBA/2% CS	Control	17.8±2.6
-	1 month	22.6±3.2	-	1 month	19.9±2.2
-	2 months	29.7±3.8	-	2 months	22.5±2.4
-	3 months	32.7±5.8	-	3 months	25.8±3.2
-	4 months	48.8±4.3	-	4 months	32.8±3.5
-	6 months	60.5±8.9	-	6 months	40.7±4.5
DGEBA/2% MCC	Control	25.5±2.1	HDGEBA/2% MCC	Control	13.8±3.4
-	1 month	30.7±2.3	-	1 month	33.5±3.5
-	2 months	37.8±2.5	-	2 months	34.7±3.7
-	3 months	42.5±3.3	-	3 months	40.4±3.2
-	4 months	62.4±3.5	-	4 months	47.2±4.5
-	6 months	75.7±2.6	-	6 months	53.5±6.7

Before exposure, DGEBA epoxy showed a high hydroxyl index value (30.6±3.4%) than those of the DGEBA/0.5% MWCNT, DGEBA/2% CS, and DGEBA/2% MCC were 19.8±1.7, 20.5±2.7%, and 32.5±2.5%, respectively. After six months exposure, the increase of hydroxyl indices of DGEBA/0.5% MWCT, DGEBA/2% CS, and DGEBA/2% MCC were decreased by 32.6%, 55.5%, and 39.1%, respectively, compared to that of the increase in hydroxyl index of DGEBA epoxy sample.

In another research, the DGEBA epoxy samples exposed to 200 h accelerated weathering cycle (UV irradiation and moisture), the chemical changes of epoxy investigated for the carbonyl and hydroxyl indices. The results of this work found out that the carbonyl and hydroxyl indices of epoxy samples slightly raised with increasing the exposure to 200 h by comparing to that of the control sample [315]. In comparison with this study, another work showed that the change in the hydroxyl index was increased from 36% to 127% in the absence of OFA filler and 40% to 46% in its presence, where a 93% reduction in the hydroxyl index was seen [314].

In another the effect of accelerated weathering on the chemical changes of DGEBA resin in the presence and absence of 5% clay filler was investigated, it found no significant improvement in the rate of oxidation over 360 h of accelerated weathering (UV exposure). The values for the area under the normalised carbonyl region of the spectrum of curve of 16.5 for DGEBA epoxy and 19 for the epoxy composite after this time (note that this must have been the increase in the area, as a value of ‘0’ is quoted at zero time, at which point there is a significant area under the curves reported as shown in Figure 4.7 [200].

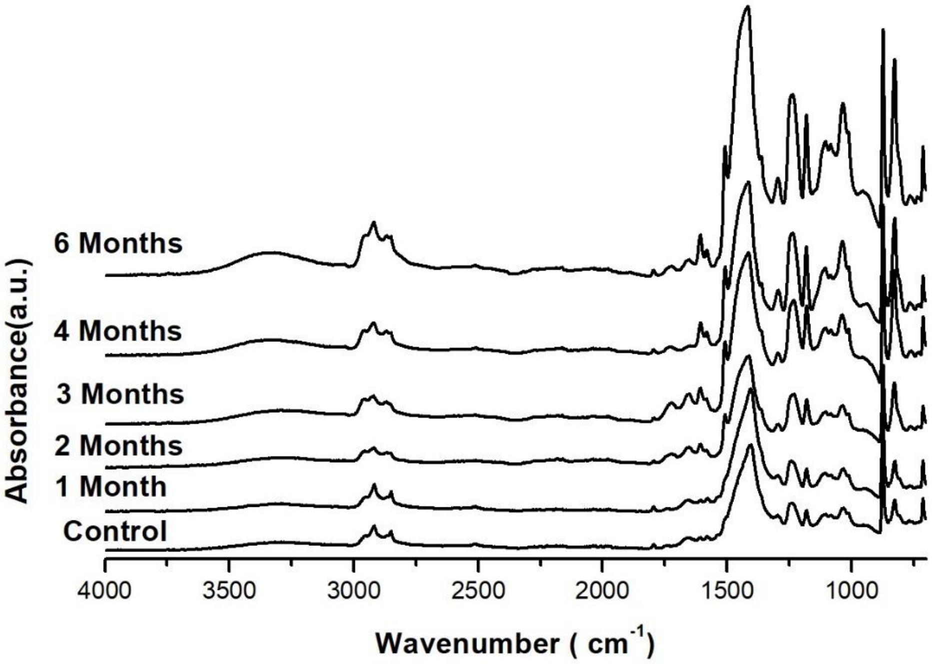


Figure 4.1: ATR- FTIR spectra comparison of DGEBA epoxy before and after exposure to different accelerated weathering times

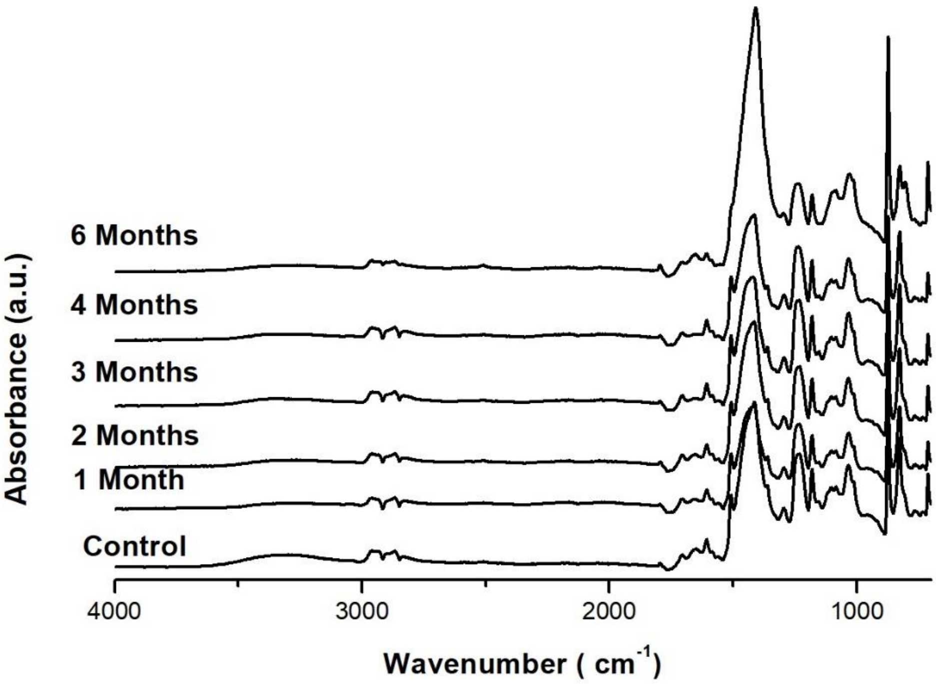


Figure 4.2: ATR-FTIR spectra comparison of DGEBA/ 0.5% MWCNT composites before and after exposure to different accelerated weathering times

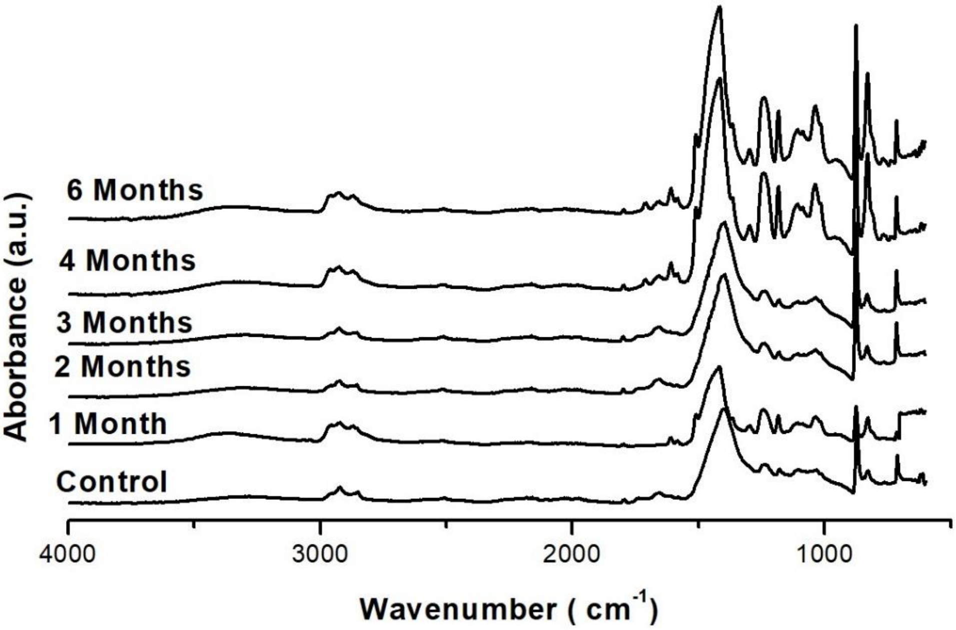


Figure 4.3: ATR-FTIR spectra comparison of DGEBA /2% MCC composites before and after exposure to different accelerated weathering times

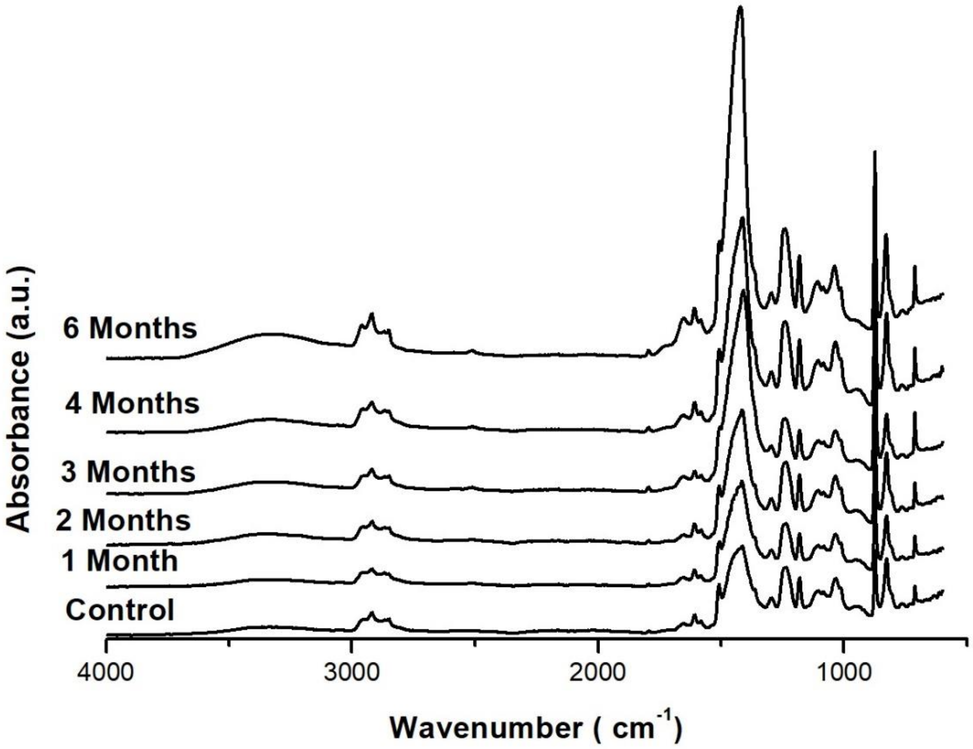


Figure 4.4: ATR-FTIR spectra comparison of DGEBA/2% CS composites before and after exposure to different accelerated weathering times

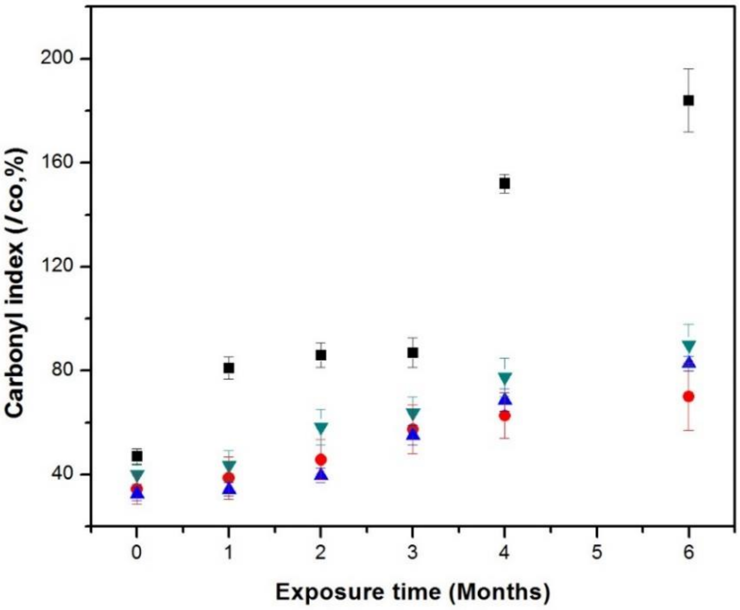
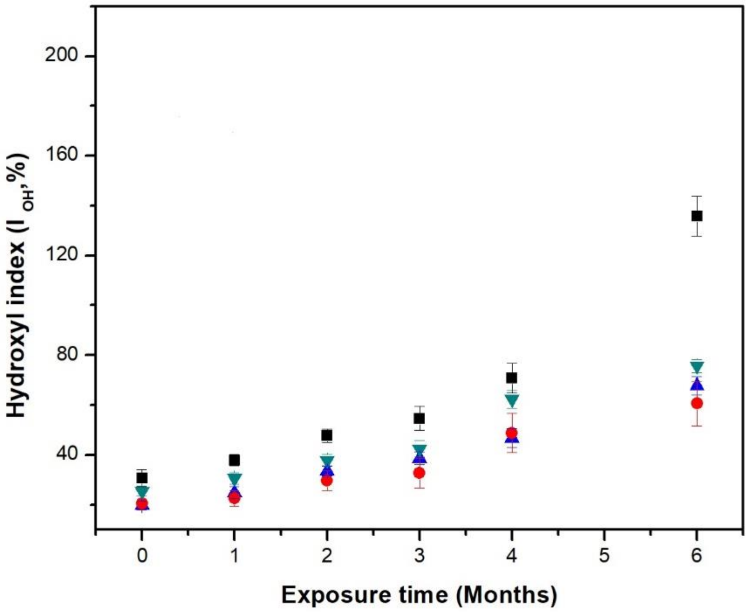


Figure 4.5: Carbonyl indices of epoxy resin DGEBA (■), DGEBA/0.5% MWCNT (●), DGEBA/ 2% MCC (▼) and DGEBA/ 2% CS (▲) before and after exposure to different accelerated weathering



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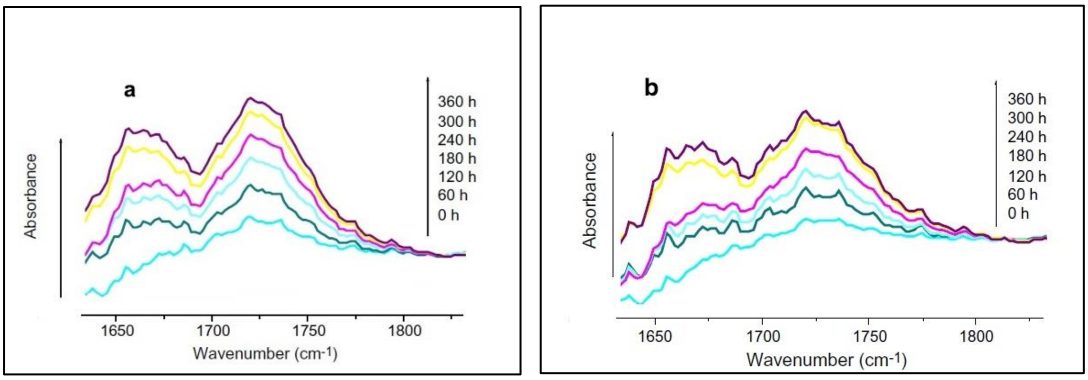

Figure 4.7: FTIR spectra for (a) neat epoxy (DGEBA) and (b) DGEBA/5 wt.% clay nanocomposite after different accelerated weathering durations [200]

From Figures 4.5, 4.6 and Table 4.1, the overall results showed that carbonyl and hydroxy indices of DGEBA epoxy and DGEBA composites increased with further increasing of exposure time. The carbonyl index of HDGEBA showed a lower increase (59±7%) than that of DGEBA epoxy (136±8%) after the exposure up to 6 months (Table 4.2). The 2% CS and 0.5% MWCNT fillers into epoxy resins were more effective in reducing the increase in carbonyl and hydroxyl indices compared with that of 2% MCC filler into epoxy resins. The DGEBA/2% CS and DGEBA/0.5% MWCNT showed lower carbonyl and hydroxyl indices, which the CS and MWCNT may be more effective to increase the crosslinking density of

DGEBA epoxy resin. With longer duration of exposure, the hydroxyl indices of DGEBA/0.5% MWCNT and HDGEBA/2% CS exhibited lower increase to around (68±4%) and (61±9%) while the DGEBA/MCC increased about (76±3%). These results showed that 2% CS and 0.5% MWCNT incorporation in DGEBA epoxy resins are more effective than that of DGEBA/2%MCC in reducing the increase of carbonyl and hydroxyl indices. The reason may be due to the small surface area and light of MWCNT filler.

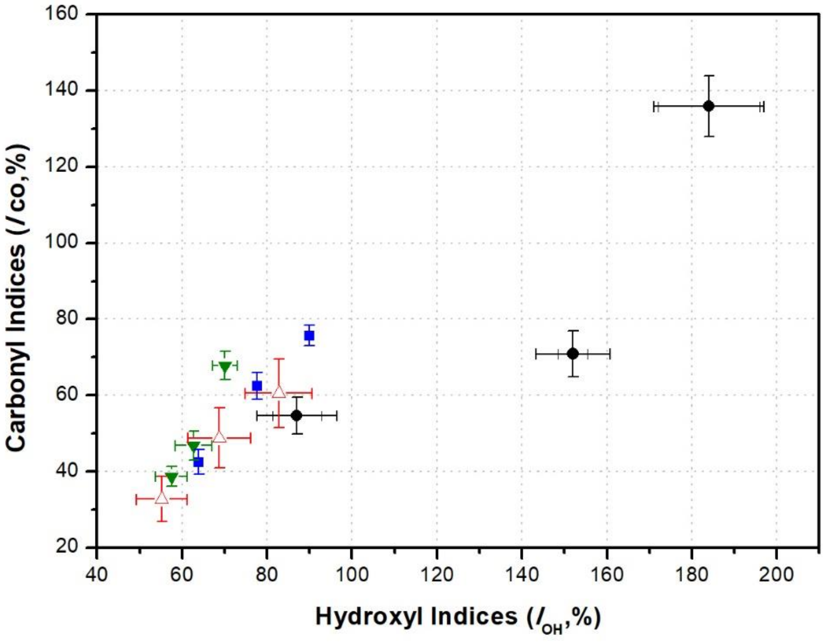

Figure 4.8: The carbonyl vs hydroxyl indices correlations of HDGEBA (●), HDGEBA/0.5% MWCNT(▼), HDGEBA/2%CS (▲), and HDGEBA/2% MCC(■) composites before and after exposure to different accelerated weathering times

4.2 Chemical Degradation of HDGEBA and HDGEBA Composites by FTIR

The FTIR analysis of HDGEBA epoxy and epoxy composite systems (HDGEBA/0.5%MWCNT) obtained before and after exposure to different accelerated weathering (0, 1, 2, 3, 4, and six months) are shown in Figures (4.9-4.12). FTIR spectra of the surface of samples exposed to different durations (1, 2, 3, 4 and six months) detected an increasing relative intensity of a hydroxyl group in the 3300 cm^{-1} bands and a carbonyl group in 1654 cm^{-1} (Figures 4.12 and 4.13). Before exposure to accelerated weathering, the carbonyl indices of HDGEBA /0.5% MWCNT, HDGEBA/2% CS, and HDGEBA/2% MCC were 20.5±2.6%, 22.4±2.8%, and 30.7±3.4%, respectively, by comparing to that of HDGEBA epoxy (34.5±5.7%). Figure 4.12 showed that no significant changes were observed in the absorption of carbonyl groups after exposure to one, two, and three months accelerated weathering for HDGEBA composite samples compared to that of DGEBA epoxy that exhibited a high value of carbonyl index. After four and six months of exposure, the carbonyl indices increased slightly for HDGEBA/0.5%MWCNT, HDGEBA/2% MCC and HDGEBA/2% CS composites (Figure 4.12). In general, HDGEBA/0.5%, MWCNT composites showed less increase in carbonyl index (20.5±2.6%) after exposure to six months accelerated weathering by comparison with that of HDGEBA epoxy (50.4±9.1%) as are shown in (Figure 4.12 and Table 4.1). After exposure to different accelerated weathering times, the hydroxyl indices were reduced for all samples (HDGEBA epoxy and HDGEBA composites), compared to those of control samples. The hydroxyl indices showed no significant changes after exposure to one, two, and three months by comparing with those of the amounts of HDGEBA epoxy (Figure 4.13 and Table 4.2).

The carbonyl and hydroxyl indices indicated overall that on a molecular level, HDGEBA/0.5% MWCNT composites exhibited a higher resistance than other composite samples to the UV irradiation, temperature, and moisture conditions. Overall results showed that the carbonyl and hydroxyl indices of HDGEBA epoxy, having more resistance to reduce the absorbance intensity. However, the HDGEBA composites exhibited no significant changes of carbonyl and hydroxyl indices during the exposure to one, two, and three months compared to that of DGEBA composites. After six months of accelerated weathering, the HDGEBA epoxy composites exhibited a lesser increase in carbonyl and hydroxyl indices compared with DGEBA epoxy composites. Before exposure, the hydroxyl index of HDGEBA/2%MCC was low (13.8±5.4%); however, after one month, exposure showed a significant decrease (33.5±3.5%). The hydroxyl indices of HDGEBA/0.5% MWCNT and HDGEBA/2% CS were 17.8±2.6% and 20.7±1.2%, respectively, in comparison to that of the HDGEBA epoxy (22.4±2.7%).

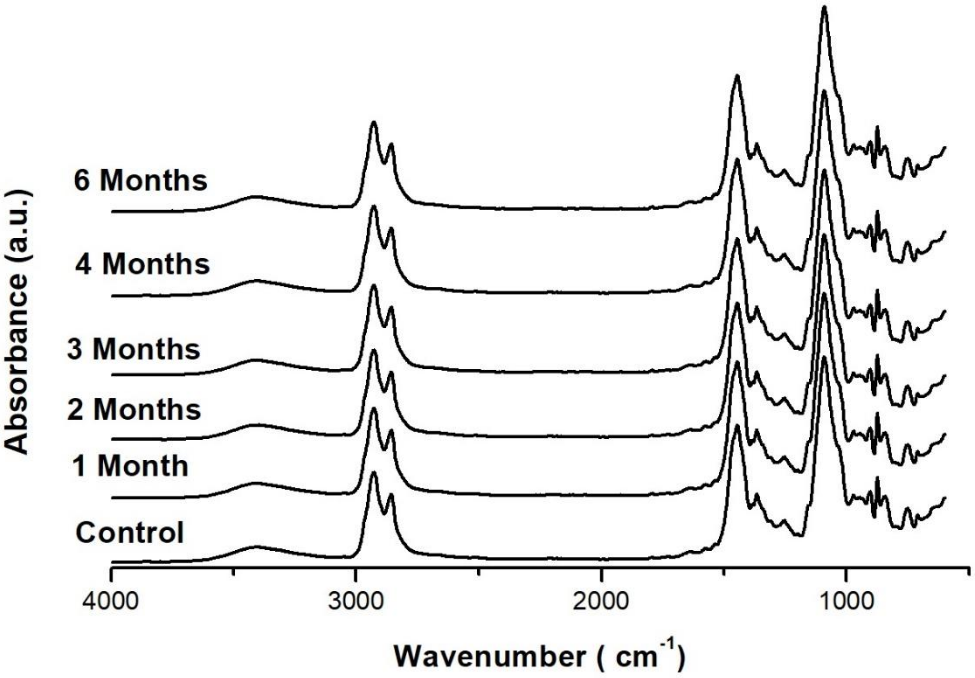

Figure 4.9: ATR-FTIR spectra comparison of HDGEBA epoxy before and after exposure to different accelerated weathering times

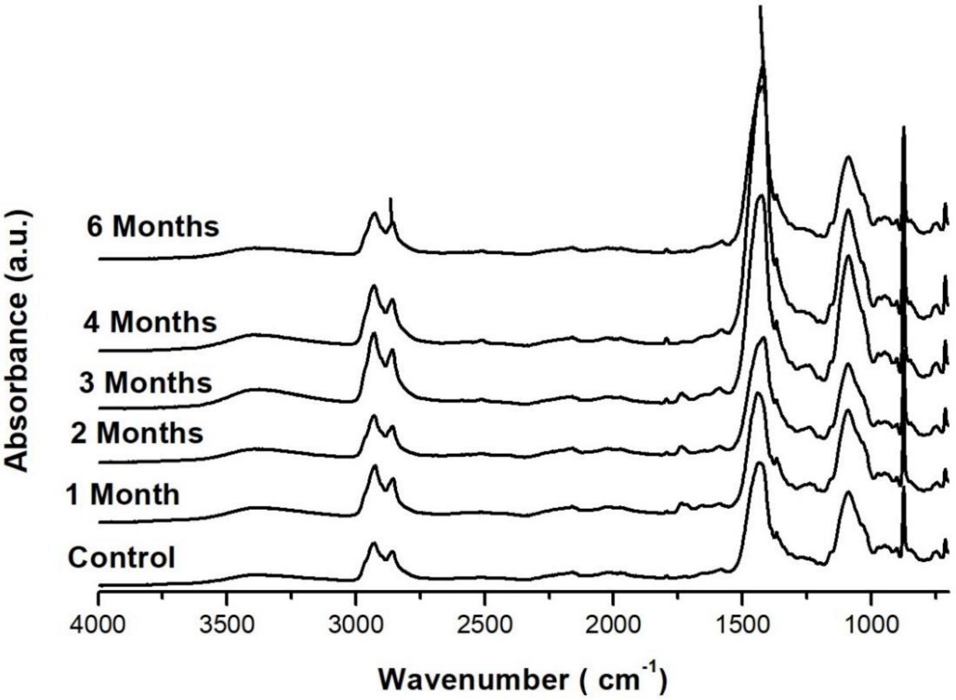

Figure 4.10: ATR-FTIR spectra comparison of HDGEBA/0.5% MWCNT before and after exposure to different accelerated weathering times

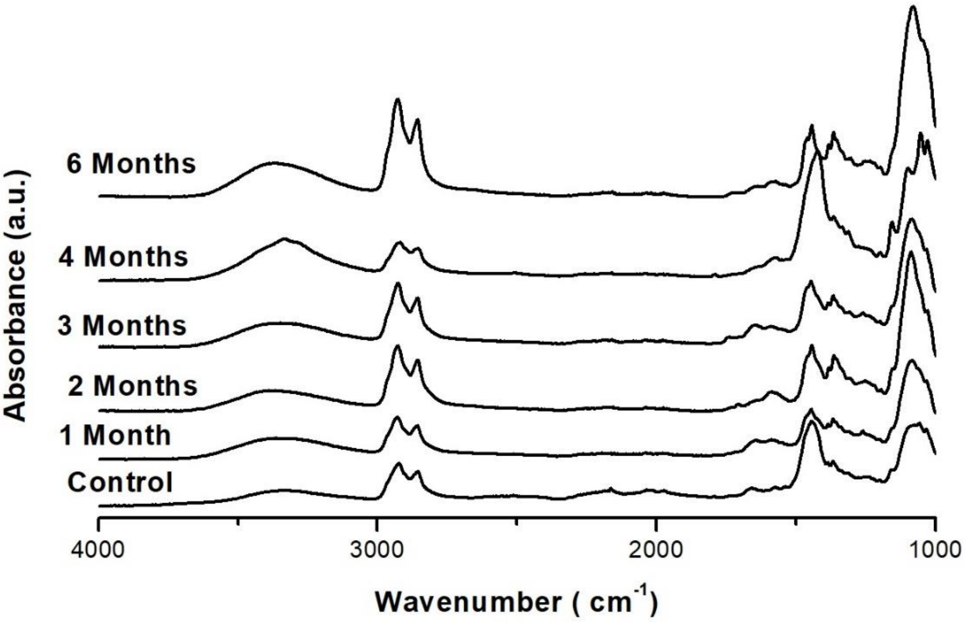

Figure 4.11: ATR-FTIR spectra comparison of HDGEBA/2% MCC before and after exposure to different accelerated weathering times

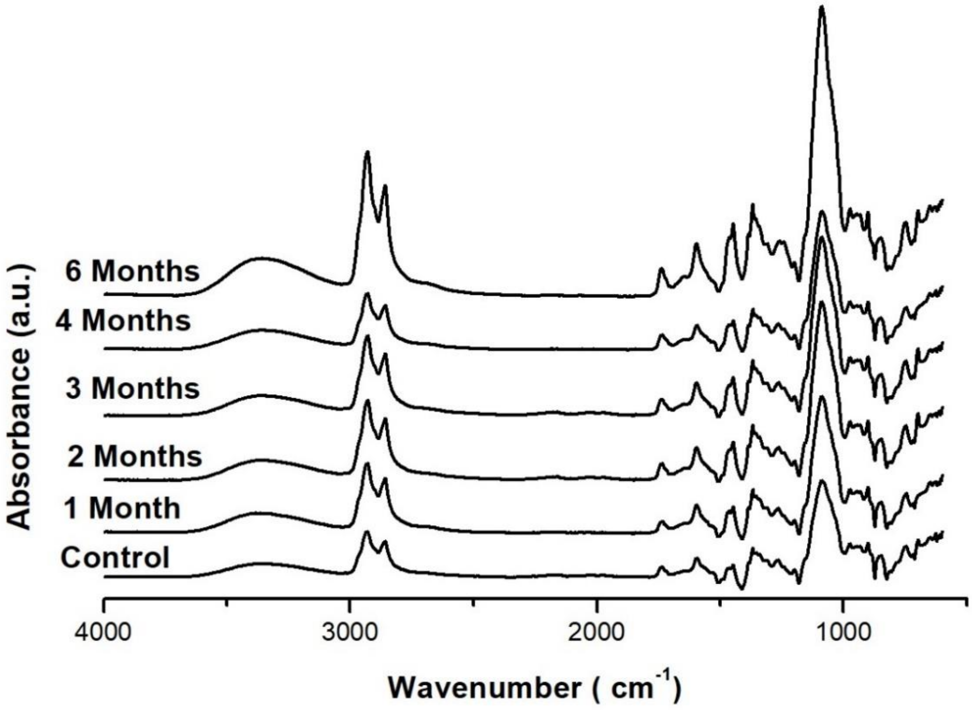

Figure 4.12: ATR-FTIR spectra comparison of HDGEBA/2% CS before and after exposure to different accelerated weathering times

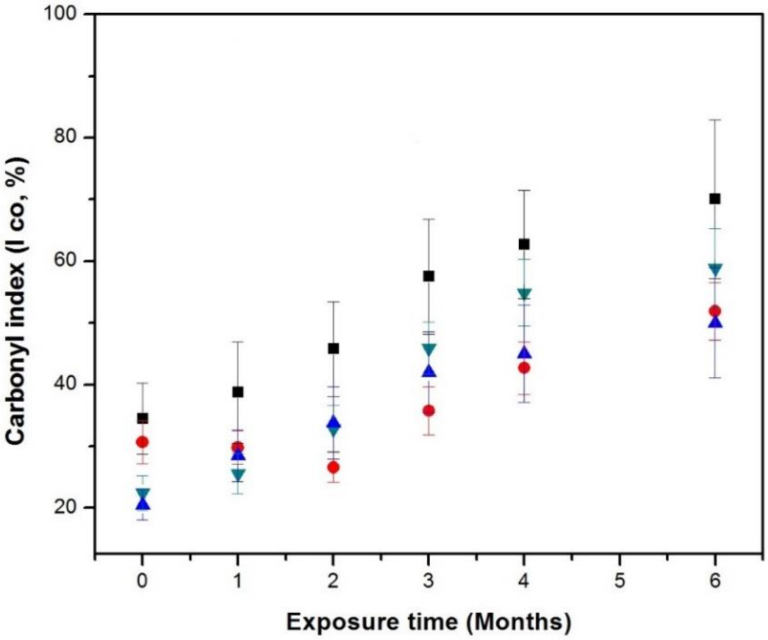

Figure 4.13: Carbonyl indices of HDGEBA (■), HDGEBA/0.5% MWCNT (▲), HDGEBA/2% MCC (▼), and HDGEBA/2% CS (●) before and after exposure to different accelerated weathering times

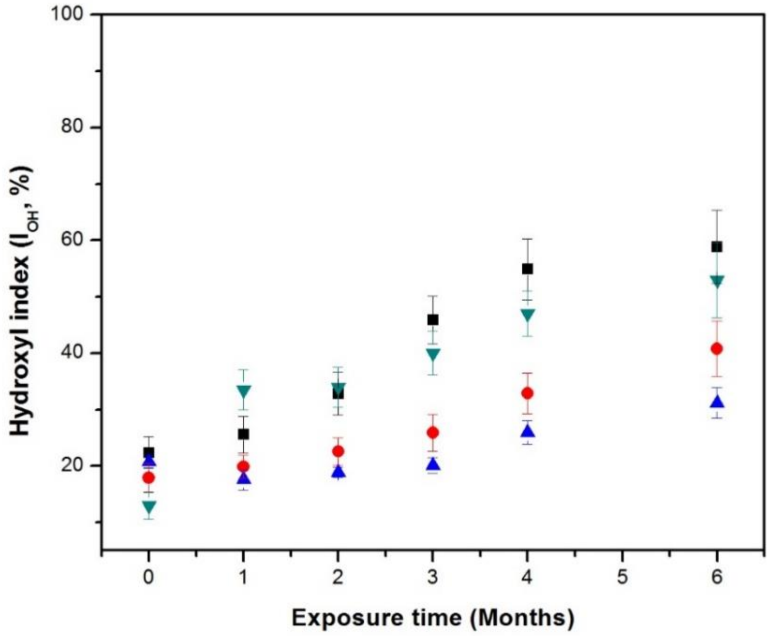

Figure 4.14: Hydroxyl indices of epoxy resin HDGEBA (■), HDGEBA/0.5% MWCNT (▲), HDGEBA/2% MCC (▼), and HDGEBA/2% CS (●) before and after exposure to different accelerated weathering times.

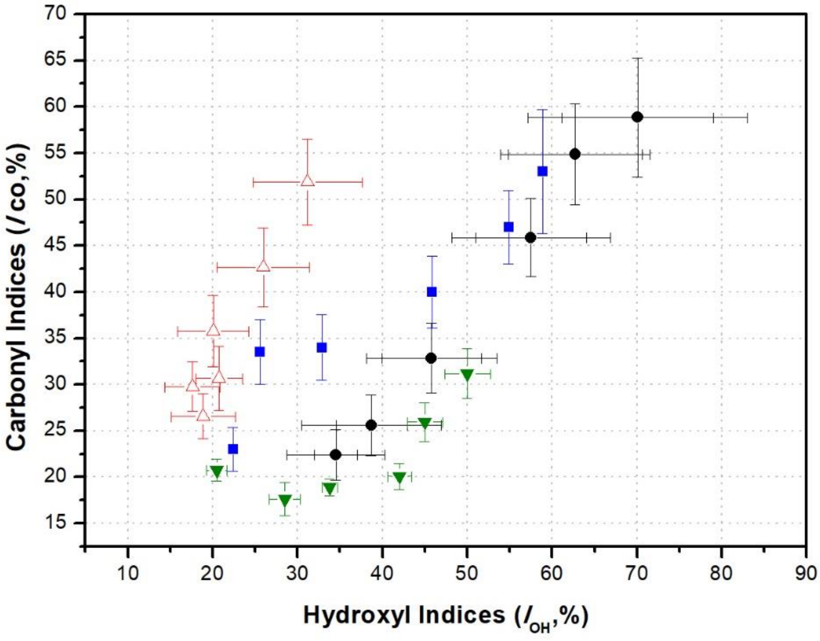

Figure 4.2: Correlation curve of carbonyl indices vs hydroxyl indices of HDGEBA (●) HDGEBA/0.5% MWCNT (▼), HDGEBA/2% CS (▲), and HDGEBA/2% MCC (■) before and after accelerated weathering

4.3 General Discussion

The results of overall chemical degradation showed that the incorporation of 0.5% MWCNT and 2 %CS in epoxy resins (DGEBA and HDGEBA) had similar effects of decreasing the surface degradation as tested by ATR-FTIR. Both DGEBA and HDGEBA without filler resulted in the carbonyl index and hydroxyl indices decreased with increasing the exposure time of accelerated weathering. However, the hydroxyl index of samples exhibited more decrease than carbonyl index of both the DGEBA and HDGEBA after exposure. This may be due to the higher formation of carbonyl groups resulting from oxygen attack of the ether groups or methylene groups linking the two phenyl groups. From the overall results obtained of carbonyl and hydroxyl indices, may be due to the 0.5% MWCNT and 2% CS additives being incorporated in epoxy resins showing more adhesion and hence the crosslinked between the fillers and epoxy resins chains [270, 276]. After six months exposure, the carbonyl indices of DGEBA/0.5% MWCNT, DGEBA/2% CS, DGEBA/2% MCC displayed a higher reduction (70±13%, 82.7±3%, and 90±8%) in comparison with DGEBA (184.4±12.4%). While the carbonyl indices of HDGEBA/0.5% MWCNT, HDGEBA/2% CS and HDGEBA/2% MCC were reduced by (50.4±9%, 53.7±6.2%, and 56±4.6%) in comparison to that of HDGEBA epoxy (70±13%).

The quantitative effects after degradation were significantly different (carbonyl and hydroxyl groups indices) between the fillers incorporated DGEBA and HDGEBA epoxy resins. From the overall results, the photo-degradation resistant performance of HDGEBA/2% CS and HDGEBA/0.5% MWCNT composites are much better than the other corresponding samples (DGEBA/2% CS and DGEBA/0.5% MWCNT) after accelerated weathering (UV light and moisture). This may suggest that the presence of CS and MWCNT fillers into HDGEBA form more effective with cross-linking between the molecules of aliphatic epoxy (HDGEBA) and molecules of CS and MWCNT and may delay the moisture diffusing out of the samples and inhibit the increase in the absorbance during UV exposure and reduce the harmful impacts of moisture on degradation intensities [200]. The overall results of the FTIR tests showed that the hydroxyl and carbonyl indices were less increase in the HDGEBA, HDGEBA/2%CS, and HDGEBA/0.5%MWCNT composites compared to those of DGEBA and DGEBA composites. The higher crosslinking density between the epoxy and MWCNT inhibited the degradation as is shown in FTIR results of carbonyl and hydroxyl indices in Chapter 4. From the overall results of carbonyl and hydroxyl indices, the HDGEBA with the added 2% CS and 0.5% MWCNT revealed lower carbonyl group absorbance, which means a lesser degradation degree compared to HDGEBA/2% MCC, HDGEBA, DGEBA, and DGEBA composites. This indicates that the addition of MWCNT and CS into an epoxy system displays excellent durability resistance and good application prospects.

From all of the results presented in Chapter 4, the UV weathering resistance of the epoxy composites was considerably affected by the kind of additional reinforcement used. FTIR analysis demonstrated that significant changes to the surface chemistry of the composite material after exposure, are observable. After six months, the characteristic peaks of C=O and O-H groups clearly increased. The HDGEBA composites, with the incorporation of 0.5% MWCNT and 2% CS showed the highest stability during the entire weathering duration and exhibited a synergistic effect on the retardation of the photo-oxidative aging of the epoxy layers, which confirmed their UV-shielding and inhibiting the increase of moisture. These results provided a theoretical reference for the development of epoxy composites for outdoor use, which have better photostability.

Chapter 5: Mechanical Testing

The tensile testing was conducted to evaluate the impact of accelerated weathering on the mechanical properties of the epoxy resins [316]. The influence of the environmental conditions (UV and moisture) in epoxy matrices and epoxy composites with three fillers on mechanical properties was tested by studying the tensile strength and elongation at break [316]. It was hypothesised [314] that epoxy network would be damaged, with chain scissions, by exposure to UV radiation and moisture exposure, hence reducing the mechanical performance of the epoxy resins.

The significance of differences in the mechanical properties between exposed and unexposed samples at different exposure periods was identified utilising statistical analysis, which will be discussed with more details at the end of this chapter.

5.1 Tensile Tests of DGEBA and HDGEBA Epoxy Resins

Typical tensile stress-strain curves of DGEBA and HDGEBA epoxy samples before and after exposure to six months accelerated weathering are shown in Figures 5.1 and 5.2, respectively. It should be noted that the relatively high degree of reproducibility obtained in the shape of the curves and the maximum stresses and strains [317]. The full list of tensile stress-strain curves under the time condition (1-4 months) is shown in Appendix A along with all epoxy composites. The overall behaviour of the tensile strength and elongation at break as functions of accelerated weathering times are shown in Figures 5.3 and 5.4, respectively [318].

Before exposure, the DGEBA epoxy had a significant higher tensile strength (41.7±2.5 MPa) compared to those the tensile strength of HDGEBA samples (20.5±1.2 MPa), as shown in Figures 5.1, 5.2, and 5.3. However, the effect the exposure of six months of HDGEBA samples exhibited a small loss in the tensile strength (13.2±1.2 MPa), in comparison to DGEBA epoxy whose strength significantly decreased over this time. After four and six months' exposure, the tensile strength of DGEBA reduced to around 40 % and 45% while the tensile strength of HDGEBA decreased to around 30% and 34%. However, the short time exposure (one, two, and three months) showed a small amount of reduction in the tensile strength of both epoxy resins, as shown in Figure 5.3. The tensile strengths of DGEBA were 39±2.3 MPa, 35±2.1 MPa, and 33±2 MPa while the tensile strengths of HDGEBA were 12.2±1.8 MPa, 12±1.6 MPa, and 10.6±0.4 MPa after exposure to one, two, and three months exposure, respectively (Figures 5.1 and 5.2). All samples exposed to different accelerated weathering consistently exhibited more elongation at break than those of unexposed samples for both epoxy resin types (Figure 5.4). In this regard, before exposure, the elongation at break of DGEBA and HDGEBA epoxy resins were (1.84±0.03%) and (4.6±0.3%), respectively, while after six months' exposure, HDGEBA epoxy samples exhibited a higher elongation at break (7.5 ± 0.3%), than did the DGEBA samples (2.8 ± 0.2%), as shown in Figure 5.4 [318].

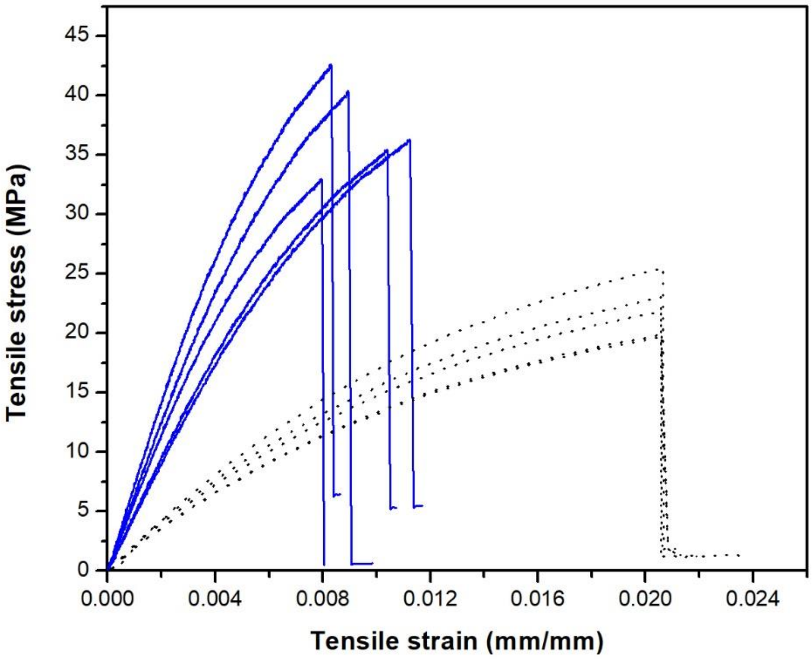

Figure 5.1: Five replicated tensile stress-strain curves of DGEBA before (solid line) and after six months (dotted line) exposure to accelerated weathering

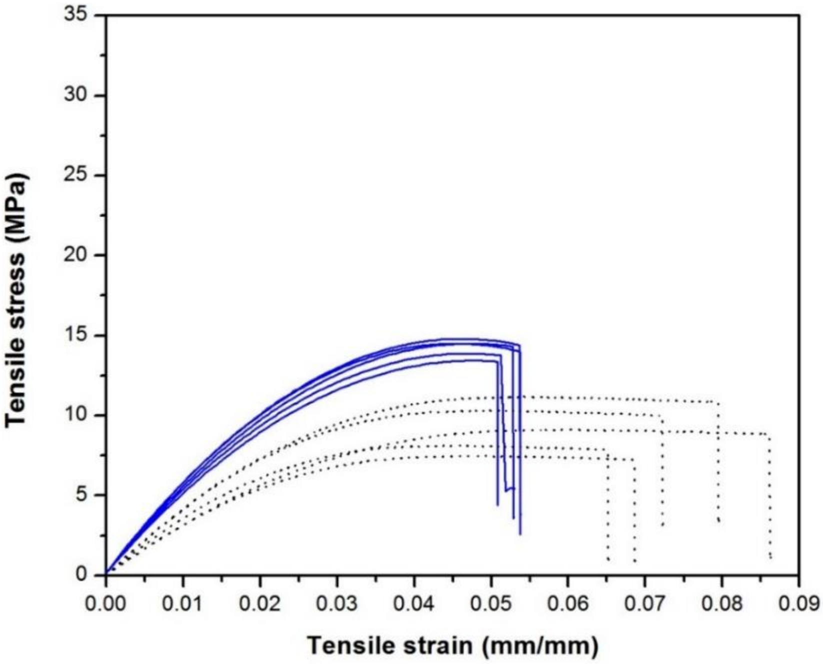

Figure 5.2: Five replicated tensile stress-strain curves of HDGEBA before (solid line) and after six months (dotted line) exposure to accelerated weathering

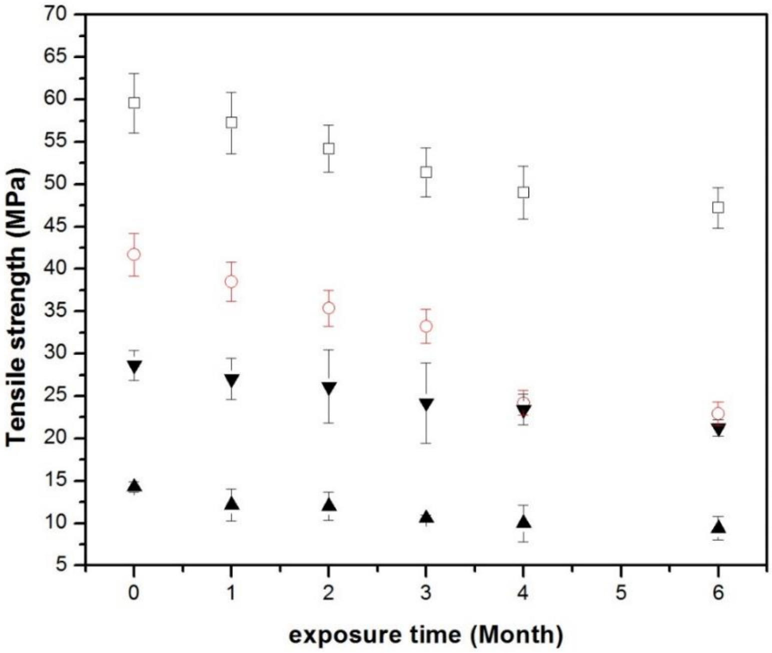

Figure 5.3: Tensile strength of DGEBA (○) DGEBA /0.5%% MWCNT (□) HDGEBA (▲) and HDGEBA /0.5% MWCNT (▼) before and after exposure to accelerated weathering

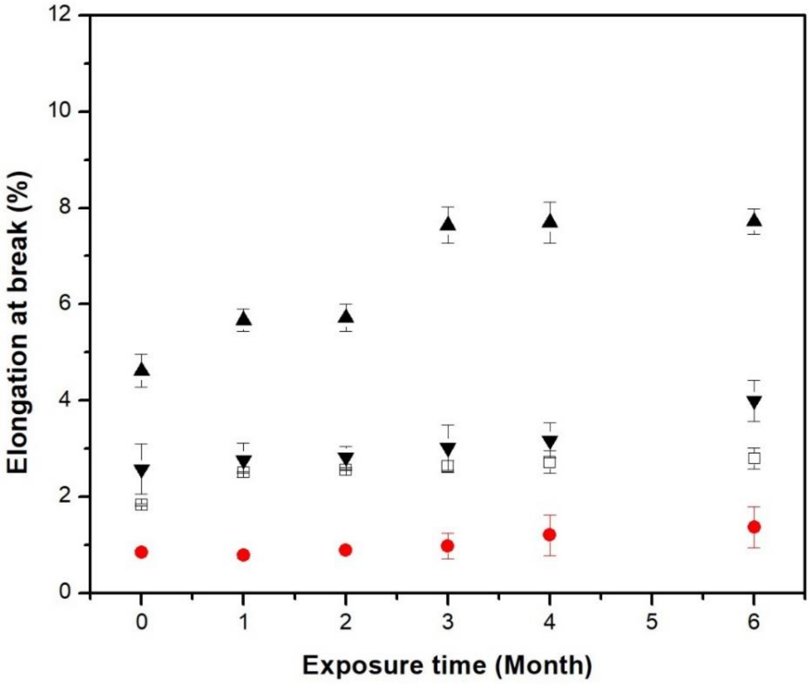

Figure 5.4: Elongation at break of DGEBA (□) DGEBA /0.5% MWCNT (●) HDGEBA (▲) and HDGEBA /0.5% MWCNT (▼) before and after exposure to accelerated weathering

5.2 Tensile Tests of Epoxy Resins/MWCNT Composites

The tensile stress-strain curves of the DGEBA/0.5%MWCNT and HDGEBA/ 0.5% MWCNT composites before and after six months' exposure to accelerated weathering are shown in Figures 5.5 and 5.6, respectively. Other data points of stress-strain curves are given in Appendix A.

After six months of exposure, the tensile strength of DGEBA/0.5% MWCNT composite displayed a significant slow decrease compared with those of DGEBA epoxy specimens whose strength significantly decreased over this time. Before exposure to accelerated weathering conditions, the DGEBA/0.5% MWCNT samples had a significant higher tensile strength (57.5±2.4 MPa) in comparison to the epoxy resin specimens (41.7±2.5MPa), as shown in Figure 5.3. Though, the effect of six months' exposure of DGEBA/0.5% MWCNT samples showed only a small loss of tensile strength of (18.26±1.2%), in contrast to DGEBA epoxy resin samples (39.3±3.5%), whose strength significantly decreased over this time. All samples exposed to accelerated weathering consistently give more elongation at break than unexposed samples for both epoxy resin types (Figure 5.4) and this was consistently greater of epoxy resin than the epoxy composite containing MWNCT. Before exposure, the DGEBA epoxy had a higher elongation at break (1.8±0.02%) than the epoxy DGEBA/0.5% MWCNT samples. After exposure to one, two, and three months, the values of elongation at break of DGEBA samples were (2.5%±0.01, 2.56±0.07%, and 2.6±0.1%) while the DGEBA/0.5% MWCNTs values were (0.8±0.06%, 0.95±0.05%, and 0.97±0.3%), as shown in Figure 5.4. However, the long exposure time (four and six months), the elongation at break of DGEBA/0.5% MWCNT composites were increased by about 41%, whereas the DGEBA was increased by about 48%. From Figure 5.4, The DGEBA/0.5% MWCNT composite had lesser reduction in elongation at break (0.86±0.05%), in comparison to the DGEBA epoxy (2.8±0.2%). An increase in elongation in the break was not linear with time, with the bulk of the rise on weathering seen in the first month for epoxy resin but between the third and fourth months for epoxy nanocomposites, suggesting a protective effect of the MWCNT [270].

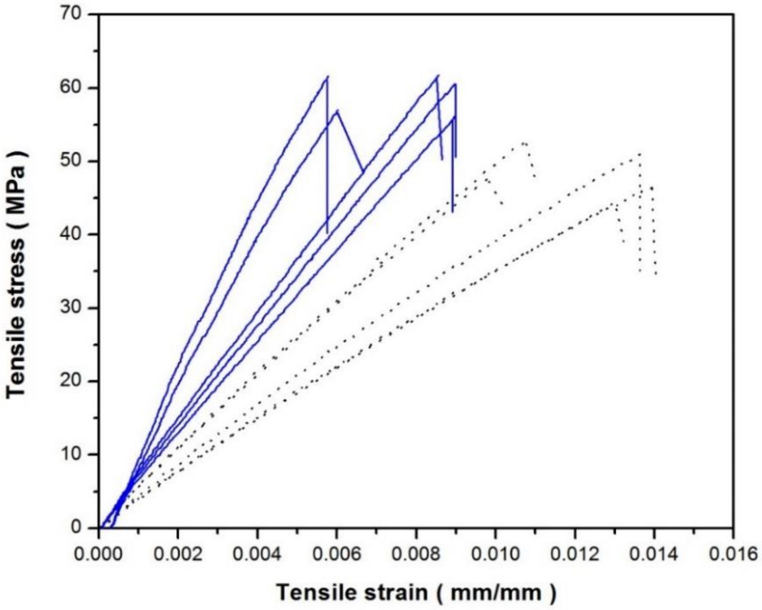

Figure 5.5: Five replicated tensile stress-strain curves of DGEBA /0.5% MWCNT before (solid line) and after six months (dotted line) accelerated weathering

Before exposure to accelerated weathering, the tensile strength of HDGEBA/0.5% MWCNT composite samples was significantly higher (27.6±2.4 MPa) than that of HDGEBA epoxy (14.5±1.2 MPa), as shown in Figure 5.3. After six months of exposure, the tensile strength of HDGEBA samples was reduced dramatically by 33 %, while the tensile strength of HDGEBA/0.5% of MWCNT composites was reduced by 20%. After exposure to one, two, and three months, the tensile strength showed that no significant reduction was shown on the HDGEBA/0.5% MWCNT samples, whereas the tensile strength of HDGEBA decreased slightly at the same times (Figures 5.3). Before exposure, the elongation at break of HDGEBA epoxy was increased by 5.5%, while after six months increased to around 7.5%. On the other hand, the incorporation of 0.5% MWCNT into HDGEBA epoxy led to lesser loss in elongation at break, 2.5% for the unexposed control sample, and 4% after exposure to six months, as shown in Figure 5.4.

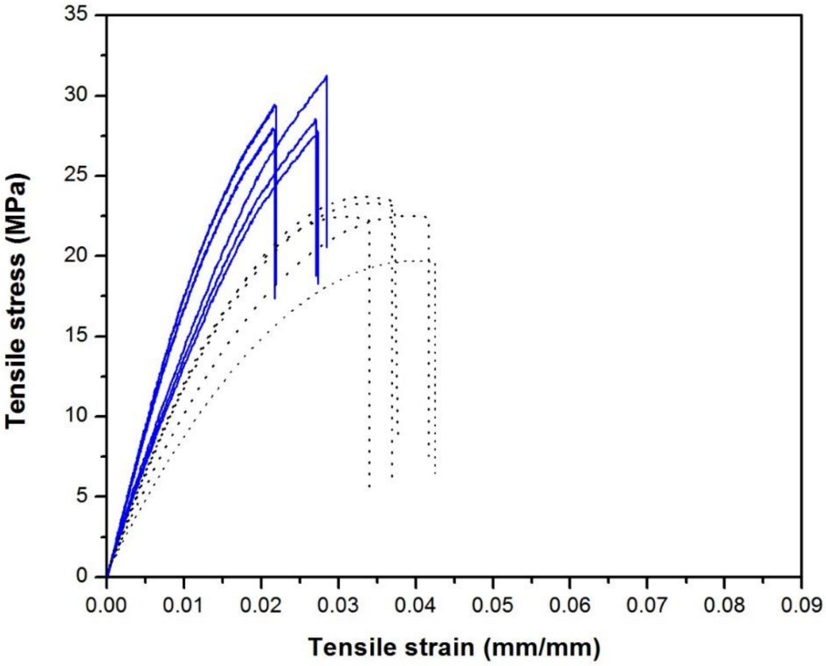

Figure 5.6: Five replicated tensile stress-strain curves of HDGEBA /0.5% MWCNT before (solid line) and after six months (dotted line) accelerated weathering

5.3 Tensile Tests of Epoxy Resin/MCC Composites

Tensile measurements were performed to assess the effect of accelerated weathering on the mechanical properties of epoxy composites. Figures 5.7 and 5.8 show the stress-strain comparison curves of DGEBA/2% MCC and HDGEBA/2% MCC composites before and after six months' exposure to accelerated weathering and other data points for other exposure times are presented in Appendix A. Note the relatively high degree of reproducibility both in the shape of curves obtained and the maximum stress and strain. Before accelerated weathering DGEBA/2%, MCC composites had the highest value of tensile strength; it was about 28±1.2% higher than DGEBA epoxy, approximately 71±3.5% greater than HDGEBA epoxy and

60±3.2% than HDGEBA/2% MCC composite, respectively (Figures 5.9). Before exposure, the DGEBA/2% MCC composites had significantly higher tensile strength (51±2.4 MPa) than the tensile strength of HDGEBA/2% MCC composite specimens (20.5±1.2 MPa). After six months of exposure, the tensile strength of DGEBA/2% MCC was 37.4±1.5 MPa, and for HDGEBA/2% MCC was 13.2±1.1 MPa (Figure 5.9).

Before exposure, the elongation at break of the DGEBA/2% MCC composite had a significantly a lower value (0.62%±0.0.2), compared to the HDGEBA/2% MCC composite (4.3%±0.3), as shown in Figure 5.10. For both epoxy resin species, elongation at break increased only slightly over six months of accelerated weathering time (See Figures 5.10). The elongation at break of DGEBA/2% MCC was (0.85%±0.03), whereas the HDGEBA/2% MCC was (5.5%±0.8) after exposure to six months accelerated weathering.

Changes in tensile strength on accelerated weathering were more pronounced of HDGEBA/2% MCC than DGEBA/2% MCC after exposure to UV irradiation and moisture after three months, with both species losing about a third of their tensile strength over the extension of exposure period to six months. The tensile strength of HDGEBA/2% MCC composite displayed more resistance to reduce the strength under all conditions.

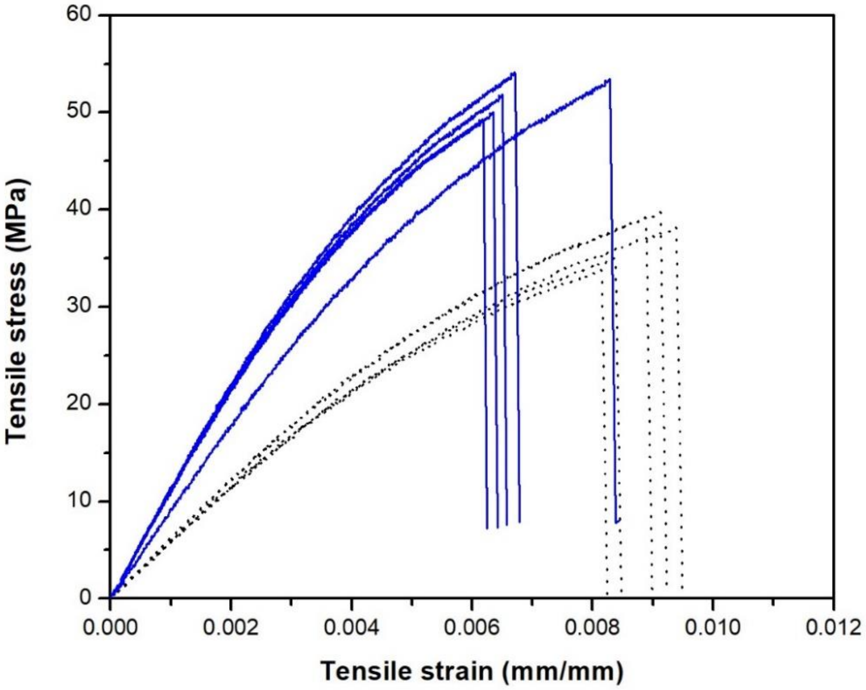

Figure 5.7: Five replicate tensile stress-strain curves of DGEBA /2% MCC composite samples before (solid lines) and after six months (dotted lines) accelerated weathering

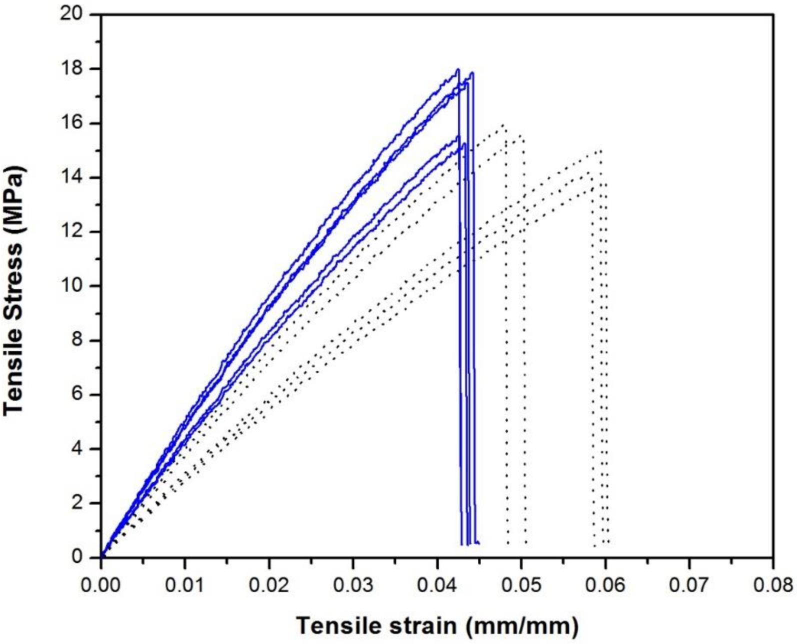

Figure 5.8: Five replicate tensile stress-strain curves of HDGEBA /2% MCC composite samples before (solid lines) and after six months (dotted lines) accelerated weathering

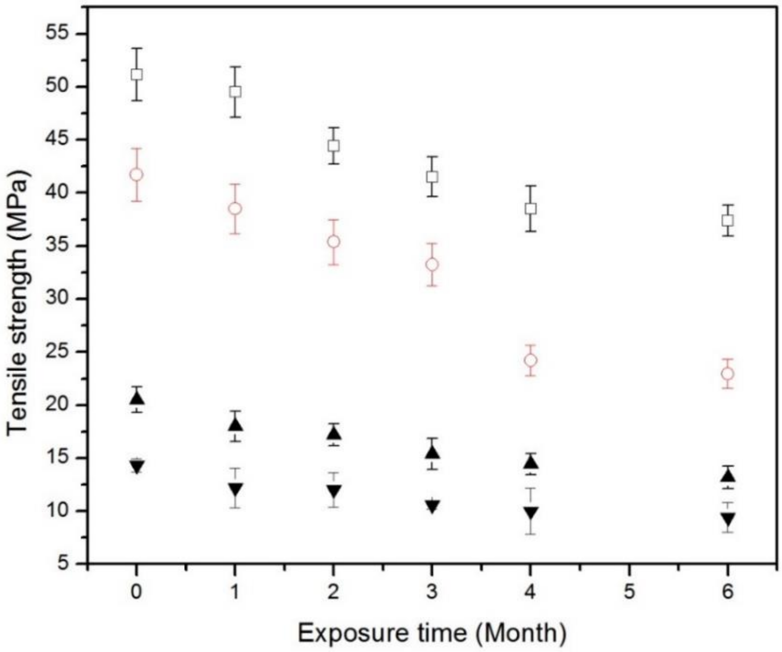

Figure 5.9: Tensile strength of DGEBA (○) DGEBA /2% MCC (□) HDGEBA (▼) and HDGEBA /2% MCC (▲) before and after exposure to different accelerated weathering times

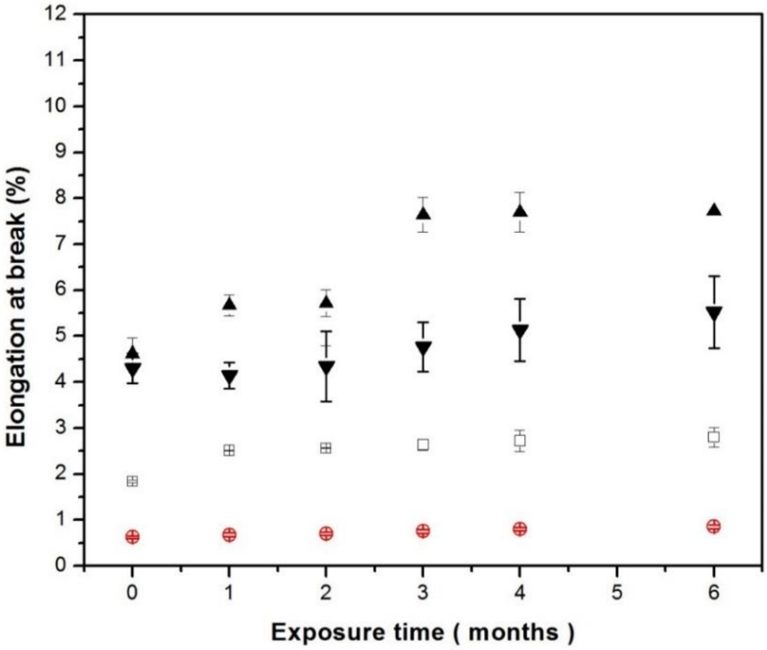

Figure 5.10: Elongation at break of DGEBA (□) DGEBA /2% MCC (○) HDGEBA (▲) and HDGEBA /2% MCC (▼) before and after exposure to different accelerated weathering times

5.4 Tensile Tests of Epoxy Resins/CS Composites

Stress-strain curves of the DGEBA/2% CS and HDGEBA/2% CS before and after exposure to six months accelerated weathering are shown in Figures 5.11 and 5.12, respectively. Before exposure, the DGEBA/2% CS composite showed the highest tensile strength (54.5±4.2 MPa), compared to that of DGEBA (42.7±3.5 MPa), whereas the HDGEBA/2% CS exhibited higher tensile strength (19.8±2.5 MPa) than the HDGEBA epoxy (13.5±1.5 MPa), as shown in Figure 5.13. However, after six months of accelerated weathering, the tensile strength of DGEBA/2% CS was reduced by 23.9±2.4%, much less than the reduction seen in DGEBA of 46.6±5.5%. After six months of exposure, the tensile strength of HDGEBA/2% CS decreased by 21.4±2.1% compared to a decrease of 28.7±1.8% for HDGEBA (Figure 5.13). These results parallel the relative effectiveness of CS in retarding the surface oxidation of two epoxy resins in demonstrating a more pronounced protective effect on the DGEBA epoxy resin.

Samples exposed to accelerated weathering consistently had a higher elongation at break values than unexposed samples for both epoxy resin and composite types (Figure 5.14). Before exposure, elongation at break was (1.84±0.12 %) for DGEBA while elongation at break for DGEBA/2% CS was of 0.65±0.09 %. After six months of exposure, the elongation at break for DGEBA was (2.8±0.2 %), compared to the elongation at break for DGEBA/2% CS that was (1.26±0.25 %). Before exposure, the elongation at break of HDGEBA/2% CS composite was (3.5±0.5 %), while HDGEBA was (4.5±0.8 %). After six months of exposure, the elongation at break for HDGEBA /2% CS was (4.8±0.7 %), while the elongation at break for HDGEBA was (7.8±0.6 %), as shown in Figure 5.14. The results of elongation at break showed that the DGEBA/2% CS composites increased to about 93.85% while the HDGEBA/2% CS composites increased to around 42.2% after the extension of six months’ exposure, this means that the HDGEBA/2% CS exhibited more resistant of the degradation to reduce the increase of elongation at break.

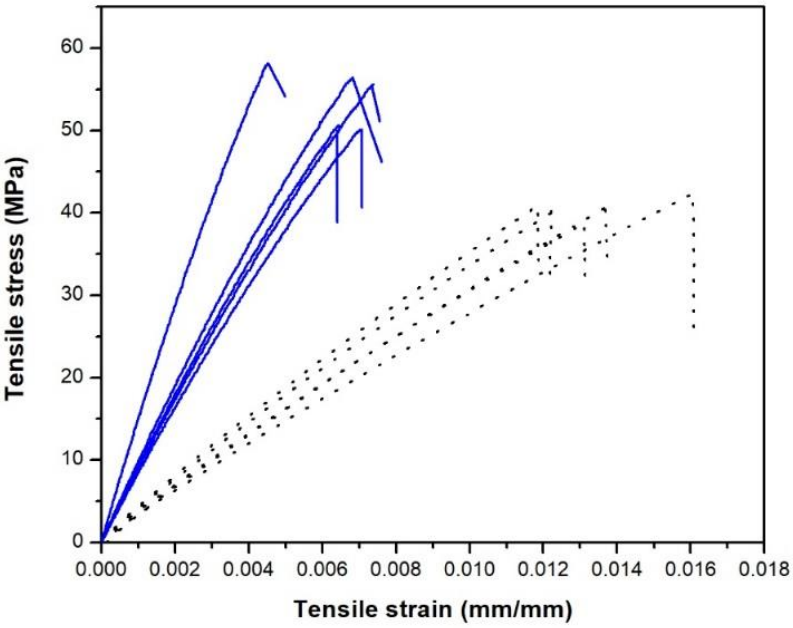

Figure 5.11: Five replicate tensile stress-strain curves of DGEBA /2% CS composite samples before (solid lines) and after six months (dotted lines) exposure to accelerated weathering

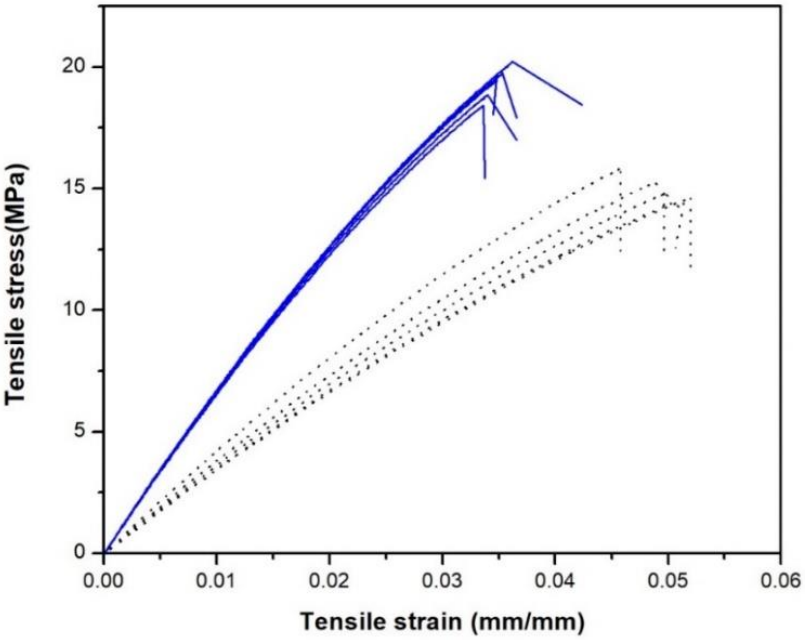

Figure 5.12: Five replicate tensile stress-strain curves of HDGEBA /2% CS composite samples before (solid lines) and after six months (dotted lines) accelerated weathering

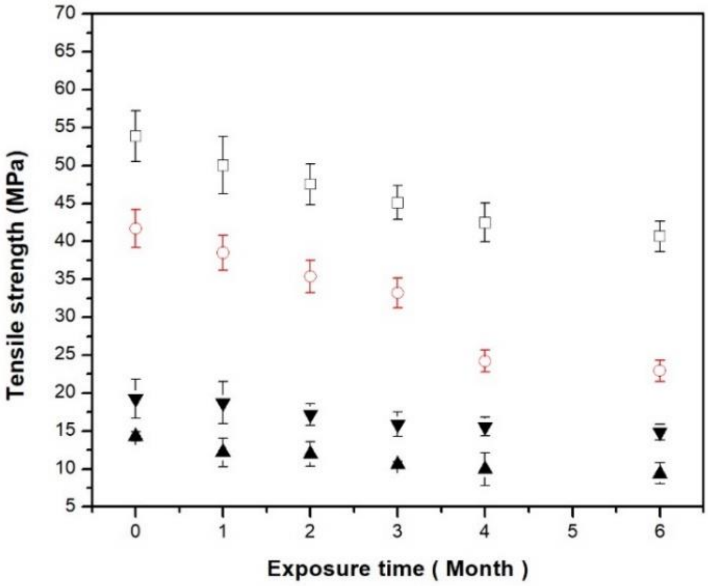

Figure 5.13: Tensile strength of DGEBA (○), DGEBA /2% CS (□) and HDGEBA (▲), HDGEBA /2% CS (▼) before and after exposure to different weathering times

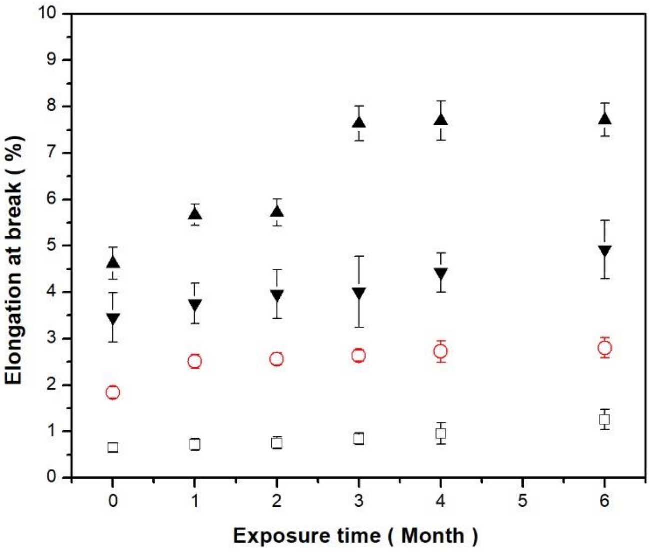

Figure 5.14: Elongation at break of DGEBA (○), DGEBA /2% CS (□) and HDGEBA (▲), HDGEBA /2% CS (▼) before and after exposure to different weathering times

5.5 DMA of Epoxy Resin and Epoxy/0.5% MWCNT

The storage modulus represents the elastic properties or energy storage ability of the composites, and the loss modulus reflects the viscous behaviour or the energy dissipation ability of composites [314]. Damping properties (Tan δ) of epoxy and epoxy nanocomposites are defined by the ratio of energy dissipated (loss modulus) to energy stored (storage modulus). The DMA measurements were carried out on one type of epoxy composite (MWCNT reinforced with DGEBA epoxy) in order to show the mechanical changes with temperature during the extension to a long time of exposure (six months). Before and after exposure to six months, typical DMA curves of epoxy resins (DGEBA) and epoxy nanocomposite (DGEBA/0.5% MWCNT) are shown in Figures 5.15 and 5.16, respectively, where storage modulus and Tan δ for each sample are plotted as a function of exposure time. Before exposure, the storage modulus of epoxy nanocomposites (DGEBA/0.5% MWCNT) was 13500 MPa while DGEBA epoxy resin was 7000 MPa. Before exposure, the peak of loss factor (Tan δ) of the DGEBA/0.5% MWCNT shifted to a higher temperature with a lower value of Tan δ (0.62) compared to that of Tan δ of epoxy resin (DGEBA), which was (0.75), as shown in Figure 5.15 and 5.16.

After exposure to six months, a significant reduction was observed in the storage modulus (37.4%) of epoxy resin (DGEBA), as shown in Figure 5.15 while the DGEBA/0.5% MWCNT nanocomposite was reduced by 8.6% (Figure 5.16). From the loss factor curves are shown in Figures 5.15 and 5.16, it can be seen that the epoxy nanocomposites (DGEBA/ 0.5% MWCNT) displayed lower amplitude peaks than that of epoxy resin (DGEBA). The loss factor (Tan δ) of DGEBA epoxy was 1.4 (Figure 5.15), whereas the DGEBA/0.5%MWCNT was 0.82, as shown in Figure 5.16. These results confirmed that the improvements of preventing the accelerated degradation of incorporation 0.5% MWCNT into DGEBA epoxy noticed after six months' exposure [317].

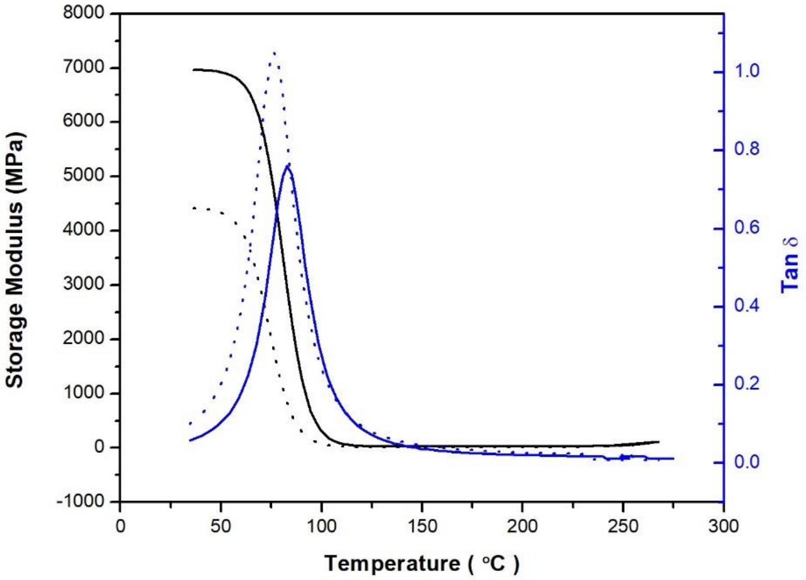

Figure 5.15: Storage modulus and loss factor (tan δ) curves for DGEBA epoxy before (solid line) and after six months (dotted line) exposure to accelerated weathering

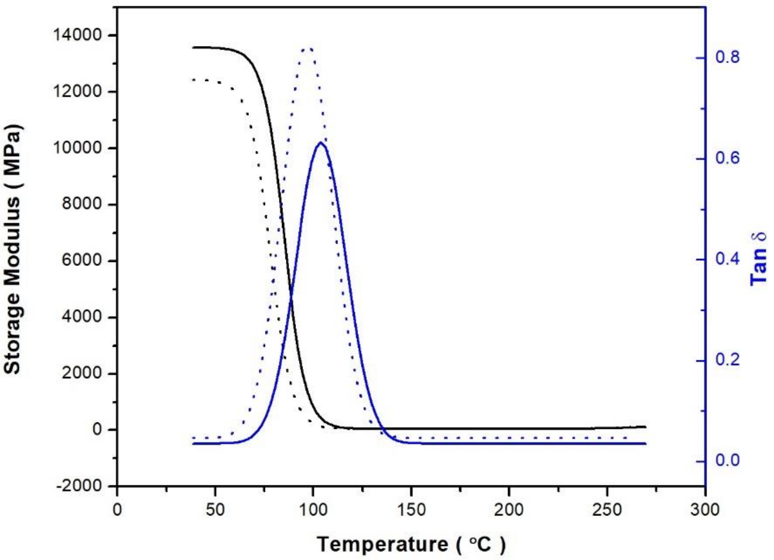

Figure 5.16: Storage modulus and loss factor (tan δ) curves of DGEBA/0.5% MWCNT nanocomposite samples before (solid line) and after six months (dotted line) exposure to accelerated weathering

5.6 General Discussion

From overall mechanical tests, all samples displayed a decrease in the tensile strength as the accelerated weathering exposure times increased. From all stress-strain curves presented in this chapter, the DGEBA/0.5% MWCNT sample has higher peak stress and a lower strain at failure.

It is evident from tensile strength curves that the DGEBA/0.5%MWCNT, and DGEBA/2% CS have the highest tensile strength (47.2±2.4 MPa and 42.7±3.5 MPa) compared to those of all samples before exposure. However, the tensile strength of HDGEBA/0.5% MWCNT and HDGEBA/2% CS composites showed less reduction in the tensile strength than the HDGEBA/2%MCC after exposure to longer exposure time (six months). The DGEBA/0.5% MWCNT showed higher tensile strength than DGEBA/2% CS, DGEBA/2% MCC, HDGEBA/0.5% MCWNT, HDGEBA/2% CS, and HDGEBA/2% MCC. The results suggest that the DGEBA/2% MCC showed poor adhesion between the MCC filler and the epoxy matrix compared with those of DGEBA/2% CS and DGEBA/0.5% MWCNT. In early exposure of accelerated weathering, there was no significant loss in tensile strength for HDGEBA/2% CS and HDGEBA/0.5% MWCNT composites compared with the corresponding DGEBA resin. After exposure to six months, DGEBA/2% MCC and HDGEBA/2% MCC composites displayed more loss in the tensile strength compared to that of DGEBA/2% CS, DGEBA/0.5% MWCNT and HDGEBA/2% CS, and HDGEBA/0.5% MWCNT composites. Shanmugam et al. [308] investigated the effect of accelerated weathering on the mechanical properties of the DGEBA/OFA composite. They concluded that the extension of exposure period to six months, the control epoxy showed a significant reduction in tensile strength (24%) compared to the corresponding epoxy before exposure, while epoxy matrix with 4 wt.% fly ash filler showed a much smaller reduction in tensile strength for the same period of exposure (15%) while in this study, the tensile strength of DGEBA/0.5% MWCNT, DGEBA/2% MCC, and DGEBA/2% CS reduced by 14%, 26%, and 23.9%, respectively.

Another study [251] showed that the tensile strength and elongation at break of epoxy resins incorporated into UV absorber (Tinuvin 1130) exhibited only a slight reduction after 800 h of UV irradiation. Tensile strength and elongation at break of epoxy resins were reduced by 30% and 35%, respectively, for a control epoxy resin after 800 h of UV exposure. In the presence of UV absorber, the tensile strength was increased by 31%, in comparison, this research work, the tensile strength of DGEBA/0.5% MWCNT, DGEBA/2% CS, and DGEBA/2% MCC composites were reduced by 23%, 25%, and 29.5%. In fact, the results obtained from mechanical tests indicated that the loss in mechanical properties of epoxy resins was reduced after incorporation of fillers.

Shanmugam et al. [314] reported that the storage modulus of control epoxy resins displayed a higher reduction by 10.59% than the 4 wt. % OFA-filled epoxy system after exposure to six months accelerated weathering.

The DMA of DGEBA and DGEBA/0.5% MWCNT showed less loss in storage modulus compared to those control sample (DGEBA) after exposure to six months. This proved that 0.5% of MWCNT prevents the accelerated degradation process of epoxy resin [315]. The results of mechanical properties presented showed that the HDGEBA and HDGEBA composites exhibited higher resistance to increase the mechanical degradation and provided more stiffness on the surface of HDGEBA and HDGEBA composites. Although the HDGEBA and HDGEBA composites exhibited fewer values of tensile strength before exposure, however; among the epoxy composite samples, the HDGEBA and HDGEBA/0.5% MWCNT and HDGEBA/2% CS composites possessed lowest losses of tensile strength after the extended to accelerated weathering exposure. This may be attributed to the mechanical degradation typically is caused by excessive brittleness of chain crosslinking and are reduced the strength by chain scission between the molecules of epoxy resins.

Before exposure, the elongation at break of HDGEBA and HDGEBA composites exhibited higher values compared to those of DGEBA and DGERBA composites. However; after exposure, the elongation showed more resistance by comparing to DGEBA and DGEBA composites. The results that were obtained from tensile tests showed that elongation at break of epoxy composite samples was slightly increased with increasing the radiation time. However; the incorporation of 0.5 % MWCNT exhibited a lower increasing compared to other samples. In fact, the presence of MWCNT into HDGEBA causes more crosslinking of chain scission reactions and the presence of carbon can decrease this affected degradation. Thus, regulating the carbon amount can be a technique to protect the epoxy composites against the degradation. Furthermore, the results obtained in this chapter suggest that the presence of 0.5% MWCNT and 2% CS into the epoxy matrix inhibits the environmental degradation and suitable stabilisers in the initial exposure.

Chapter 6: Thermal Degradation

Thermal gravimetric analysis is one the most significant measurements to estimate the behaviour of thermal stability of polymers or epoxy resins, particularly when they are exposed to different environmental impacts. The measurements of TGA of epoxy resin and epoxy composites provide important information to follow, in terms of the weight loss of a polymer or an epoxy as a function of temperature is determined before and after exposure to accelerated weathering. The weight loss at the maximum temperature (T_{max}), which is obtained from the differential thermogravimetric (DTG) curves provides a significant point about the thermal degradation after exposure to different accelerated weathering [319].

6.1 TGA Analysis of Epoxy Resins

Thermal degradation of DGEBA and HDGEBA epoxy resins was followed by TGA and DTG analysis in order to compare the thermal stability of two epoxies before and after exposure to different accelerated weathering times (Table 6.1). Typical thermograms curves of all samples are given in Appendix B. The thermal stability of each composition was followed based on the values of the initial decomposition temperature (T_{i}), the maximum decomposition temperature (T_{max}) and the residual mass of the exposed and control (DGEBA and HDGEBA) samples, which are summarised in Table 6.1. Before accelerated weathering, HDGEBA specimens had a higher initial decomposition temperature (T_{i} = 410 °C), than DGEBA samples (T_{i} = 395 °C) (Table 6.1). The initial of decomposition temperature showed significant decreases with increasing the time of exposure, more so with DGEBA (341 °C) than HDGEBA (365 °C) after six months of exposure to accelerated weathering. After exposure to one, two, and three months, there were slight decreases for both DGEBA and HDGEBA. After exposure to one month, two months, three, and four months, The T_i of DGEBA was 357.7 °C, 354.4 °C, 353.5 °C, and 352.5 °C while the T_i of HDGEBA was 372.2 °C, 373.5 °C, 368.1 °C, and 367.4 °C. There were no observed changes in the weight loss of both two epoxies. The T_{max} of the two epoxies also decreased with increasing the exposure to one to four months. The T_{max} values of DGEBA were 394.1, 392.4, 384.5, and 379.4 while T_{max} values of HDGEBA were 408.5 °C, 406.1 °C, 399.5 °C, and 398.2 °C after exposure to one, two, three, and four months, respectively as shown in Tables 6.1 and 6.2. Before exposure, the rate of mass (residual mass, %) of DGEBA was 25.3% while HDGEBA was 36.5%. After exposure to six months, it was noticed that the rate of mass loss of HDGEBA was decreased by 14.3% while the DGEBA was lower (7.1%) as shown in Tables 6.1 and 6.2. The improvement of thermal stability of HDGEBA samples after exposure due to the high crosslinking density between the aliphatic epoxy resins (HDGEBA) by the effect of degradation [318].

6.2 TGA Analysis of Epoxy Resins/MWCNT Composites

Before exposure, the DGEBA/0.5%MWCNT composite had a higher initial degradation (T_i=389 °C) than DGEBA epoxy (T_i=365 °C) as shown in Table 6.1. After exposure to one, two, and three months, there were no significant changes shown of the T_i of DGEBA/0.5% MWCNT compared with that of DGEBA epoxy. The T_{max} of the two epoxies also decreased with increasing the exposure to six months (405 °C for epoxy nanocomposite) and (375 °C for epoxy resin) (Table 6.1). The control DGEBA/0.5% MWCNT sample had more residual mass at 500 °C (42.5 %) than that of the epoxy resin before weathering (25.3%), and this trend continues to be evident after six months of accelerated weathering, although the absolute amount of residue drops as shown in Table 6.1. As this change in residual mass is vastly higher than the amount of MWCNT present in the modified sample [270], it is clear that incorporation of 0.5% MWCNT is providing a significant inhibition of thermal degradation. An earlier work to investigate the effect of incorporating of 4% oil fly ash (OFA) into DGEBA epoxy on the thermal degradation before and after exposure to six months, showed that the % residual mass of DGEBA epoxy was 4.3% while the % residual mass of DGEBA/4% OFA was 6.1%, a decrease in the amount of epoxy resin -derived residue, suggesting the reduction in extent of pyrolysis of epoxy resin observed with MWCNT is not a general phenomenon of incorporation of fillers [314, 306].

Typical thermograms curves of HDGEBA/0.5% MWCNT are shown in Appendix B. The T_i, the T_{max}, and the residual mass of HDGEBA and HDGEBA/0.5% MWCNT are summarised in Table 6.2. It can be observed that all samples before and after exposure to accelerated weathering display a one-stage decomposition process independent of the exposure time [309]. Before exposure, HDGEBA/0.5% MWCNT composite sample had a higher T_i (436.5 °C), than that of HDGEBA epoxy (410 °C) as shown in Table 6.2. The initial decomposition temperature significantly decreased with increasing the time of exposure to accelerated weathering. After exposure to one, two, and three months, there were no significant changes shown of T_i values of HDGEBA/0.5% MWCNT and HDGEBA. After exposure to four months, the T_i of HDGEBA/0.5% MWCNT was (373.1 °C) while the T_i of HDGEBA was (367.4 °C). The T_i of HDGEBA/0.5% MWCNT had a higher (T_i =369.7 °C) than HDGEBA (T_i =365 °C) after six months of exposure. The T_{max} of HDGEBA reduced from 410 °C to 390 °C while the HDGEBA/0.5% MWCNT decreased from 436.5 °C to 399.8 °C with increasing the exposure to six months (Table 6.2). After four months of exposure, the T_{max} showed no significant decrease of HDGEBA/0.5 % MWCNT (408.5 °C) compared with that of HDGEBA (398.2 °C). Before exposure, the HDGEBA/0.5% MWCNT sample had more residual mass (46.5 %) than that of HDGEBA sample (36.5%). After exposure to six months, the residual mass of

HDGEBA/0.5% MWCNT was (40%) while the HDGEBA was (14.3%), as shown in Table 6.2 [270].

Table 6.1: The data of TGA and DTG for DGEBA and DGEBA composites before and after exposure to different accelerated weathering times

Samples	Exposure time (Month)	T_i ± 0.2ºC	T_{max} ± 0.2ºC	Residual mass (%)
DGEBA	Control	365.1	395.2	25.3
	1	357.7	394.1	24.6
-	2	354.4	392.4	23.1
-	3	353.5	384.5	22.3
-	4	352.3	379.4	19.2
-	6	341.1	375.2	7.1
DGEBA /2% CS	Control	378.5	409.2	44.5
	1	376.5	405.4	43.5
-	2	371.6	397.5	37.5
-	3	367.7	392.5	26.7
-	4	362.5	388.7	23.1
-	6	359.8	383.2	22.5
DGEBA /0.5% MWCNT	Control	388.7	432.5	42.5
	1	386.5	431.2	42.1
	2	381.4	427.4	40.7
	3	376.2	418.1	39.2
	4	373.4	412.5	38.6
	6	371.1	405.4	38.4
DGEBA /2% MCC	Control	375.5	421.3	30.7
	1	373.4	417.1	28.5
	2	370.2	412.4	26.7
	3	366.5	406.3	23.1
	4	362.5	397.5	22.5
	6	358.5	391.2	19.5

6.3 TGA Analysis of Epoxy Resins/MCC Composites

The values of TGA and DTG obtained from TGA and DTG curves of poxy and epoxy composites (Appendix B) are summarised in Tables 6.1 and 6.2. Before exposure; the HDGEBA/2% MCC had a higher T_i (383.5 °C) than those of the DGEBA/2% MCC (375.5 °C), DGEBA (365 °C), and HDGEBA (372.5 °C) (Tables 6.1 and 6.2). After exposure of one, two, and there months were only limited changes in the initial temperature of both two epoxy composites. The T_i values of HDGEBA/2% MCC were 381.2 °C, 376.5 °C, and 371.2 °C while the T_i values of DGEBA/2% MCC were 373.4 °C, 370.2 °C, and 366.5 °C after exposure to one, two, and three months, respectively. However, after six months of exposure, T_i had decreased markedly for both epoxy composites, T_i of DGEBA/2%MCC was 358.5 °C while the HDGEBA/2% MCC was 362.5 °C. Before exposure, the values of T_max for DGEBA/2% MCC and HDGEBA/%MCC were 421.3 °C and 425.4 °C while after exposure to six months, the DGEBA/2% MCC and DGEBA/2% MCC were 388.5 °C and 391.2 °C (Tables 6.1 and .2). The control HDGEBA/2% MCC sample had more residual mass (35.5%) than the control DGEBA/2% MCC composite sample (30.7%), as shown in Tables 6.1 and 6.2. After six months, the residual mass of HDGEBA/2% MCC was about 29.5% while the DGEBA/2% MMC was approximately 19.5%. From Tables 6.1 and 6.2, it is clearly shown that the residual mass residue decreased with more extended periods of accelerated weathering, consistent with oxidation taking place not only on the surface but in the interior of the material, and this trend was more pronounced for the DGEBA/2% MCC composite than for the HDGEBA/2% MCC composite, suggesting that the aromatic moiety makes the epoxy resin more susceptible to degradation. These results showed that the incorporation MCC in epoxy improved the thermal resistant with long-time exposure to accelerated weathering [306]. The 2% MCC filled HDGEBA provided additional protection to reduce the thermal degradation with exposure time compared to that of epoxy without filler.

6.4. TGA Analysis of Epoxy Resins/CS Composites

Typical thermograms (TG) and their derivatives (DTG) curves of DGEBA/2% CS and HDGEBA/2% CS and the results are summarised in Tables 6.1 and 6.2. Before exposure, the T_{i} of HDGEBA/2% CS composite sample exhibited a slight increase in thermal decomposition (T_{i} =385.5 °C) compared those of DGEBA/2% CS sample (T_{i}=378.5 °C), DGEBA (365 °C), and HDGEBA (372.5 °C), as shown in Tables 6.1 and 6.2. After exposure up to four months, there were no significant changes in the initial decomposition temperature for both two epoxy composites (DGEBA/2% CS and HDGEBA/2% CS) compared to those of control epoxy samples (DGEBA and HDGEBA). However, at longer exposure times, significant differences became evident. Before exposure, the T_{max} of DGEBA/2% CS composite was 409.2 °C while the T_{max} of DGEBA was of 395 °C. After six months accelerated weathering exposure, the T_{i} of DGEBA /2% CS composite had decreased by 19.7 °C and T_{max} had been reduced by 26.0 °C while for DGEBA T_{i} had been reduced by 24 °C and T_{max} by 20 °C. Before exposure, the T_{i} of HDGEBA/2% CS was 385.5 °C, and T_{max} was 427.7 °C, while for HDGEBA initial T_{i} was 372.5 °C and T_{max} was 410 °C. After six months of exposure, HDGEBA/2% CS had a fall in T_{i} of 17.0 °C and a fall in T_{max} of 18.5 °C while HDGEBA had a fall in T_{i} of 7.5 °C and of T_{max} by 20.0 °C, as shown in Tables 6.1 and 6.2. These results recommend that there is no significant effect of CS incorporation in retarding the degradative processes, which lead to a reduction in the initial temperature of thermolysis with time, although CS may impart an initial reinforcing effect [304].

The epoxy/2%CS composites were found to be larger unpyrolysed residue than the unmodified epoxy resins before accelerated weathering (44.5% vs. 25.3% for DGEBA epoxy; 45.2% and 36.5% for HDGEBA epoxy), very much larger than the direct contribution of the calcium sulfate, suggesting a significant impact of the inorganic filler in inhibiting pyrolysis [304]. This difference appeared much higher on accelerated weathering, to a somewhat more considerable extent for DGEBA-based (35.7% vs. 7.1%) than that of HDGEBA epoxy (39.8 % vs.14.3%), as are shown in Tables 6.1 and 6.2.

The reduction in the amount of residue with more extended times of accelerated weathering is consistent with oxidation taking place not only on the surface but in the interior of the material; as this trend was more pronounced for the DGEBA composite than for the HDGEBA composite, it indicates that the aromatic moiety makes the epoxy resin more susceptible to degradation than aliphatic moiety for the epoxy resin [304].

Table 6.2: TGA data of HDGEBA and HDGEBA composites before and after exposure to different accelerated weathering times.

Samples	Exposure time (Months)	T_i ± 0.2ºC	T_{max} ± 0.2ºC	Residual mass (%)
HDGEBA	Control	372.5	410.5	36.5
	1	372.2	408.5	36.1
-	2	373.5	406.1	34.5
-	3	368.1	399.5	28.7
-	4	367.4	398.2	20.2
-	6	365.1	390.4	14.3
HDGEBA /2% CS	Control	385.5	427.7	45.2
	1	383.4	425.4	44.7
-	2	379.7	422.2	43.4
-	3	376.5	419.1	41.7
-	4	373.5	414.2	40.8
-	6	368.5	409.2	39.8
HDGEBA /2% MCC	Control	383.5	425.4	35.5
	1	381.2	422.2	34.8
	2	376.5	420.5	34.2
	3	371.4	415.4	31.5
	4	367.2	402.6	30.2
	6	362.5	388.5	29.5
HDGEBA /0.5% MWCNT	Control	385.2	436.5	46.5
	1	382.4	433.1	44.8
	2	377.5	425.1	44.2
	3	374.8	418.4	42.1
	4	373.1	408.5	40.5
	6	369.7	399.8	40.1

6.5 T_g Analysis of Epoxy Resins/MWCNT Composites

The summary of measurements of T_g from DSC curves for all the exposed and control specimens containing MWCNT are given in Table 6.3. Before exposure of accelerated weathering, the T_g value of the epoxy nanocomposites (150.5 °C) was significantly higher than the epoxy resin (120.5 °C), which is due to enhance the rate of crosslinking reaction to get larger cross density, thereby increasing the glass transition temperature. After exposure to one, two, and three months DGEBA/MWCNT composite samples did not show slight changes to reduce the T_g values (147.7 °C, 142.5 °C, and 139.2 °C), respectively, (Figure 6.2), in comparison with those of the T_g values of DGEBA for the same condition exposure times (Figure 6.1). After four months of exposure, the T_g value of DGEBA/0.5% MWCNT was (137.8 °C) while the T_g value of DGEBA was (98.2 °C), as shown in Table 6.3 and Figure 6.2. After six months of exposure, DGEBA/0.5% MWCNT had higher flexibility to reduce the degradation (135.7 °C), compared to epoxy resin samples (88.7 °C), as is shown in Table 6.3 and Figure 6.1. All the samples (epoxy resin and epoxy/0.5% MWCNT composites) show a reduction in T_g after exposure to different times as compared to the unexposed samples (Table 6.3). This demonstrates the important contribution of functionalised MWCNT to the protection of epoxy resins against the accelerated weathering exposure [270].

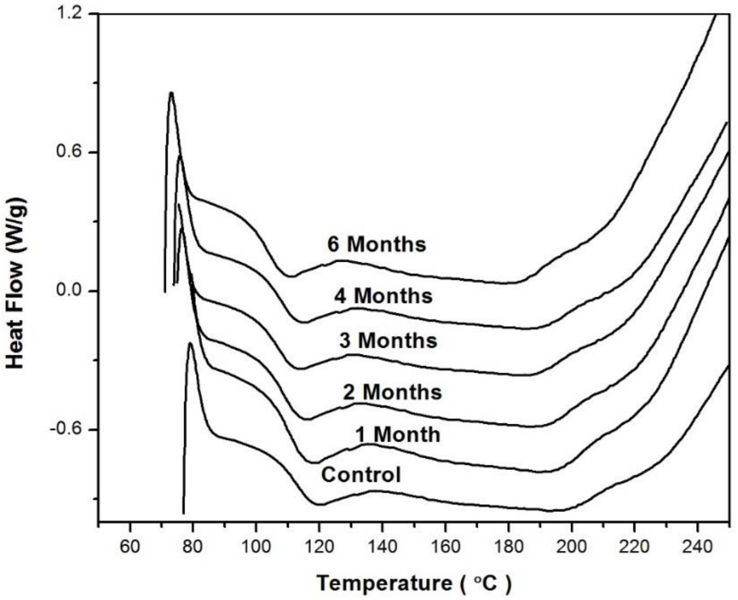

Figure 6.1: DSC thermograms of DGEBA samples before and after exposure to different accelerated weathering times

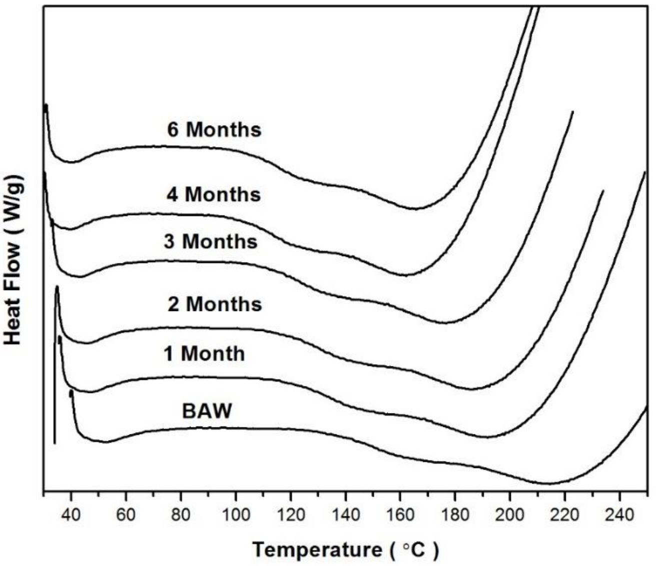

Figure 6.2: DSC thermograms of DGEBA /0.5% MWCNT composites before and after exposure to different accelerated weathering times

Figures 6.3 and 6.4 show a comparison of T_g values for HDGEBA and HDGEBA/0.5% MWCNT composites after exposure to one, two, three, four, and six months accelerated weathering. From the results in Table 6.3, it was evident that of HDGEBA/0.5% MWCNT composite had more resistance to reduce the T_g values with increasing the weathering over time. Before exposure, the T_g value of HDGEBA (97.4 °C) was slightly lower than HDGEBA/0.5% MWCNT (188 °C). After one, two, and three months, the T_g values of HDGEBA and HDGEBA/0.5% MWCNT did not show slight changes. After four months of exposure, the T_g value of HDGEBA was (92.5 °C), while HDGEBA/0.5% MWCNT was 180.4 °C. After six months of exposure, the T_g value of HDGEBA/0.5% MWCNT was 180.4 °C whereas the T_g value of HDGEBA was 188.5 °C (Table 6.3). During the accelerated weathering exposure process, the amounts of T_g were reduced and made the HDGEBA epoxy resins brittle. Hence, after six months of weathering, HDGEBA/0.5% MWCNT had higher flexibility as a result of a lower degradation process, compared to HDGEBA epoxy samples [270]. The resistance in redcution of T_g value of HDGEBA/0.5% MWCNT after exposure, maybe due to to the formation of polar groups, which can prevent chain movements and change as an internal plasticiser and reduced the mobility of polymeric chains, representing the important contribution of functionalised MWCNT to the protection of epoxy adhesives against the accelerated weathering exposure [270,320].

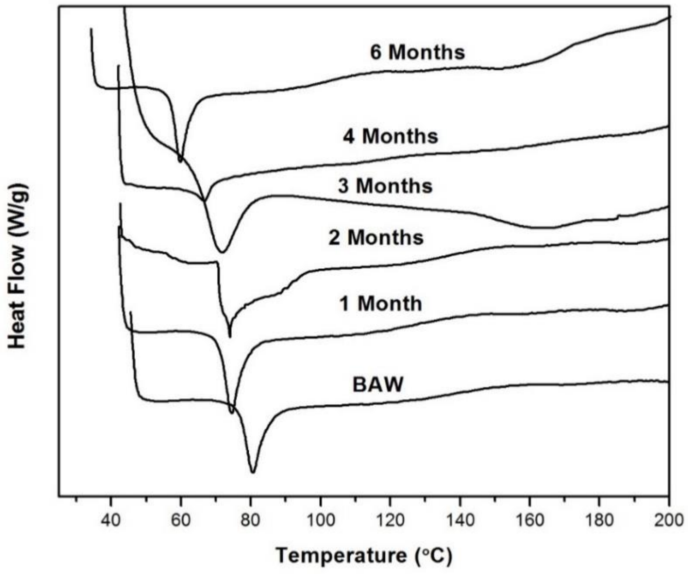

Figure 6.3: DSC thermograms of HDGEBA epoxy before and after exposure to different accelerated weathering times

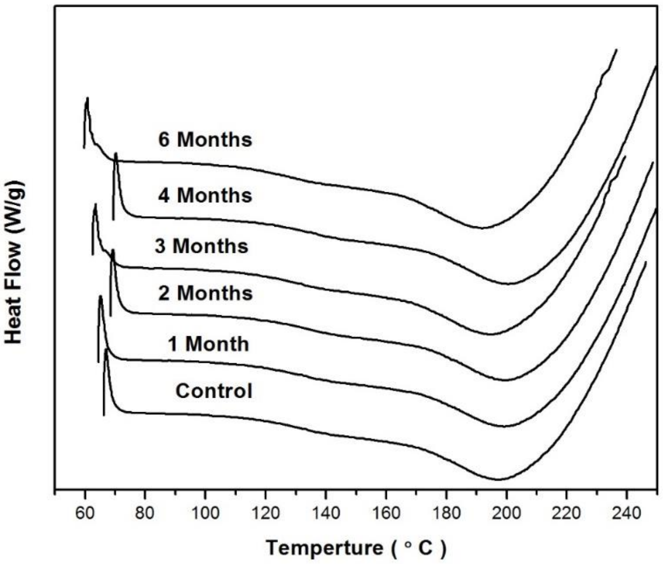

Figure 6.4: DSC thermograms of HDGEBA / 0.5% MWCNT epoxy before and after exposure to different accelerated weathering times

6.6 T_g Analysis of Epoxy Resins/MCC Composites

DSC thermograms of representative DGEBA/2% MCC and HDGEBA/2% MCC composites are given in Figures 6.5 and 6.6. The results of T_g obtained from DSC curves for epoxy resins and epoxy resins/2% CS are summarised in Table 6.3. Before exposure to accelerated weathering, the value of T_g for HDGEBA/2% MCC was 179.5 °C while the T_g of DGEBA/2% MCC was 128.5 °C, which was significantly higher than those of HDGEBA (97.4 °C) and DGEBA (120.5 °C). After exposure to one, two, and three months, the T_g values of DGEBA/2% MCC composites were 126.4 °C, 122.5 °C, 118.4 °C, respectively, while the T_g values of HDGEBA/2%MCC were 177.4 °C, 176.2 °C, and 173.4 °C. These values of T_g showed that incorporation of MCC filler in HDGEBA was increased by (80 °C), compared to that of HDGEBA before exposure (Table 6.3). After four months, the T_g value of DGEBA/2% MCC was reduced by (16 °C), while the T_g value of HDGEBA/2% MCC reduced to around 9 °C. After six months exposure, the HDGEBA/2% MCC exhibited more resistance to reduce the T_g value than DGEBA/2%MCC, the T_g value of DGEBA/2% MCC was decreased by (20 °C), while Tg value of HDGEBA/2% MCC was reduced by (14 °C), as shown in Table 6.2. From these results, it is evident that the extent of accelerated weathering significantly reduced the value of T_g for all samples.

In comparison to this work, another study was reported by Tang et al. [321], which investigated the impact of epoxy/cellulose nanocrystalline composites on the thermal stability properties (T_g). They suggested that the monomeric epoxy species, utilised in this work are covalently linking to the MCC, increasing chain immobilisation and decreasing the chain length between crosslinks and very much higher than the negligible increase of T_g observed for cellulose whisker composites with oligomeric DGEBA. However, the DGEBA/cellulose nanocrystalline composite materials have also displayed no variation in T_g at up to 0.9% [320, 306].

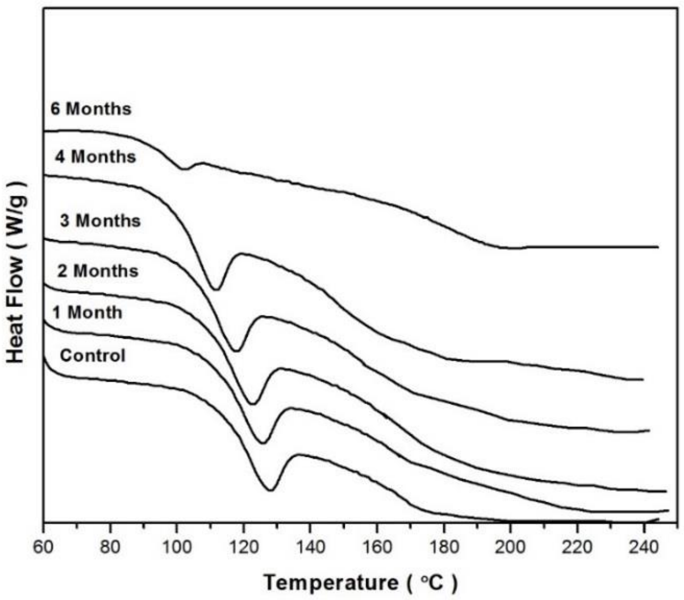

Figure 6.5: DSC thermograms of DGEBA /2% MCC samples before and during exposure to different accelerated weathering times

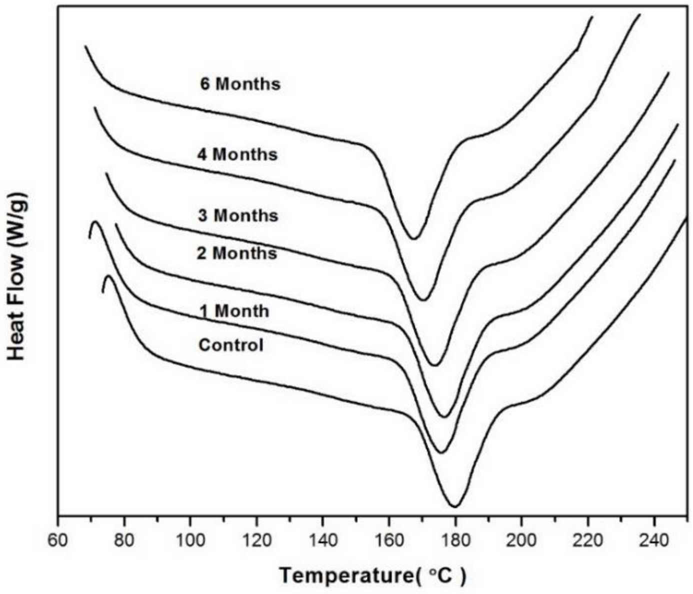

Figure 6.6: DSC thermograms of HDGEBA /2% MCC samples before and during exposure to different accelerated weathering times

6.7 T_g Analysis of Epoxy Resins/CS Composites

DSC curves for DGEBA/2% CS and HDGEBA/2% CS composites are given in Figures 6.7 and 6.8. T_g values of all the exposed specimens measured are shown in Table 6.3. Before exposure to accelerated weathering, the value of T_g of the HDGEBA was 97.4 °C, whereas HDGEBA /2% CS composite showed a higher T_g value (189.5 °C) than those of the DGEBA (120.5 °C) and DGEBA/2% CS composite samples (126.5 °C), as shown in Table 6.3. After six months of exposure, all samples showed decreases in T_g values, with T_g decreasing to around 14.0 °C for HDGEBA composites and 16.5 °C for DGEBA composites, but this was similar to or greater than the extent of decline seen for the unmodified resins, where 6.8 °C reduced T_g for HDGEBA and 31.8 °C for DGEBA epoxy. This suggests that the presence of CS has a limited effect in reducing chain scission and plasticisation over the course of accelerated weathering, although the interaction between the filler and the matrix are highly effective in reducing chain mobility.

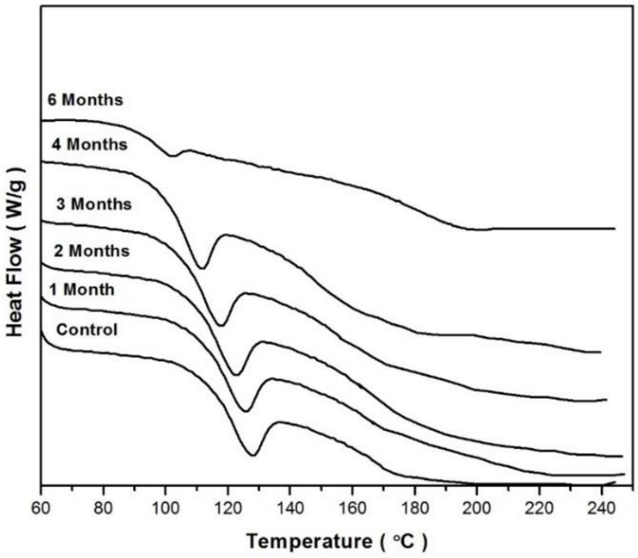

Figure 6.7: DSC thermograms of DGEBA /2%CS composite samples before and after exposure to different accelerated weathering times

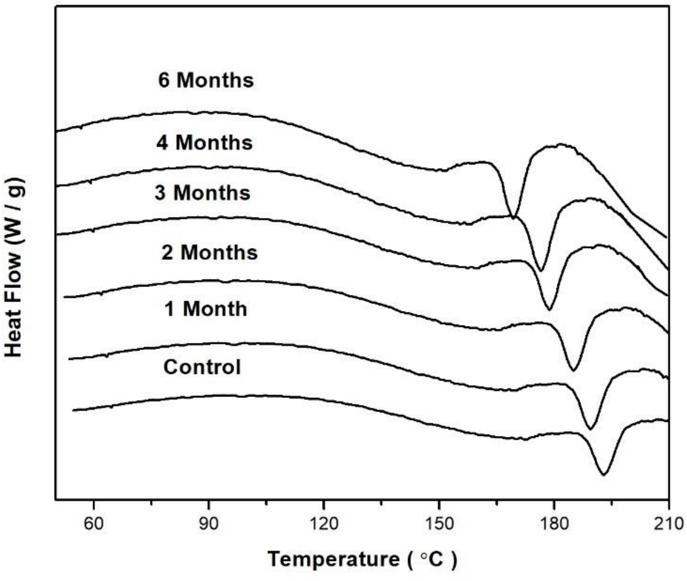

Figure 6.8: DSC thermograms of HDGEBA /2% CS composite samples before and after exposure to different accelerated weathering times

Table 6.3: The values of T_g from DSC thermograms of DGEBA, HDGEBA, and DGEBA and HDGEBA composites before and after exposure to accelerated weathering

Samples	Exposure time (Months)	T_g (°C)	Samples	Exposure time (Months)	T_g (°C)
DGEBA	Control	120.5	HDGEBA	Control	97.4
-	1	116.4	-	1	96.8
-	2	110.5	-	2	95.3
-	3	102.8	-	3	93.2
-	4	98.2	-	4	92.5
-	6	88.7	-	6	90.6
DGEBA/0.5% MWCNT	Control	150.5	HDGEBA/0.5% MWCNT	Control	188.5
-	1	147.7	-	1	188.0
-	2	142.5	-	2	187.0
-	3	139.2	-	3	185.4
-	4	137.8	-	4	184.7
-	6	135.7	-	6	180.4
DGEBA/2% CS	Control	126.5	HDGEBA /2% CS	Control	189.5
-	1	126.1	-	1	184.4
-	2	122.5	-	2	180.3
-	3	118.4	-	3	177.6
-	4	112.5	-	4	176.8
-	6	108.4	-	6	168.5
DGEBA/2% MCC	Control	128.5	HDGEBA/2% MCC	Control	179.5
-	1	126.4	-	1	177.4
-	2	122.5	-	2	176.2
-	3	118.4	-	3	173.4
-	4	112.5	-	4	170.5
-	6	108.3	-	6	165.5

6.8 General discussion

The overall results of thermal stability of epoxy resins and epoxy composites before and after exposure to different accelerated weathering times were studied by TGA and DSC analysis.

Characterisations showed that the maximum and initial temperatures of DGEBA epoxy exhibited higher values by comparing to HDGEBA epoxy before exposure. However, with more extended exposure to accelerated weathering, the HDGEBA exhibited more resistance to the thermal degradation. After six months exposure, DGEBA and DGEBA composites displayed a significant decrease in T_i, T_{max}, and the residue values, which showed lower thermal stability toward the long-time exposure if compared with those of HDGEBA and HDGEBA composites. The HDGEBA/2% CS and HDGEBA/0.5% MWCNT composites exhibited more thermal stability over exposure times than DGEBA/2% CS, DGEBA/0.5% MWCNT and epoxy resins/2% MCC. The reason may due to CS and MWCNT made more crosslinking density with epoxy matrix and good interfaces to provide more protection of epoxy resin without loss of the mass at higher temperatures. The lower rate of mass loss in the case of 0.5% MWCNT and 2% CS filled epoxy matrix is attributed to the ability of these fillers to retard the degradation of the epoxy matrix. This result showed that the presence of the MWCNT and CS as a thermal stabiliser in the epoxy composites, used for this study diminished the effects of exposure when compared to control epoxy resins.

The tests of T_g was carried out, utilising DSC technique to identify the changes in mobility of epoxy and epoxy composites chains. The overall results are presented of T_g values in this chapter are shown clearly that the systems display single T_g in the experimental temperature range from 30 to 250 ℃.

Before exposure, the incorporation of fillers in DGEBA epoxy exhibited no significant increase in T_g values and there are minor improvements to increase the T_g values, while the HDGEBA composites showed the greatest improvement to increase the T_g value, which maybe the higher interaction between and HDGEBA epoxy and fillers enhanced the crosslinking density and stiffness of composites (Table 6.3). After exposure to six months, the T_g values of 2% CS and 0.5% MWCNT into epoxy resins exhibited more resistance to reduce the increase of T_g values than the MCC into epoxy resins (Table 6.3). The HDGEBA/2% CS and HDGEBA showed lesser impact to reduce the T_g values, in comparison to the corresponding DGEBA composites. Overall results showed that MWCNT and CS fillers consider good thermal stabilisers of epoxy resins after the exposure to different accelerated weathering times and enhancing the crosslinking density of HDGEBA matrix. Briefly, the results TGA and DTG results are presented in this chapter of epoxy and epoxy composites lead to believe that the thermal degradation mechanism of HDGEBA composites is greatly retarded, compared to DGEBA composites. The reason behind this inhibition of the thermal degradation mechanism maybe due to the degradation behaviour of fillers (MWCNT, CS, and MCC) is greatly influenced by the presence of the crosslinked units of these fillers in the HDGEBA epoxy chain.

Chapter 7: Morphology Analysis

SEM images were collected to study the effect of the accelerated weathering (UV light and moisture exposure) with different exposure times on the surface morphology of epoxy and epoxy composite samples. SEM micrographs provide critical information about the fracture surface after exposure to the accelerated weathering and provide a clear idea regarding the dispersion of fillers in the epoxy matrix.

7.1 SEM Analysis of DGEBA and HDGEBA Epoxy Resins

SEM Micrographs of DGEBA and HDGEBA epoxy samples before and after exposure to three and six months accelerated weathering are displayed in Figures 7.1 and 7.2, respectively. Before exposure, the SEM image of the HDGEBA sample exhibited a smooth, glassy surface as shown in Figure 7.2A, compared to that of the DGEBA micrograph (Figure 7.1A), which showed a rough surface and micro-sized particles, or an agglomeration of curing agent distributed on the surface, which may be due to the heterogeneous distribution between the curing agent and epoxy resin. The SEM micrograph of HDGEBA (Figure 7.2B) did not display any significant change on the surface compared to the SEM micrograph of DGEBA (Figure 7.1B) after up to three months' exposure, after which showed small voids on the surface were seen over more extended periods of accelerated weathering for DGEBA epoxy. After six months of exposure, the DGEBA micrograph (Figure 7.1C) showed a significant fracture on the cross-section of the surface, while SEM micrograph of HDGEBA exhibited little fracture on its surface (Figure 7.2 C).

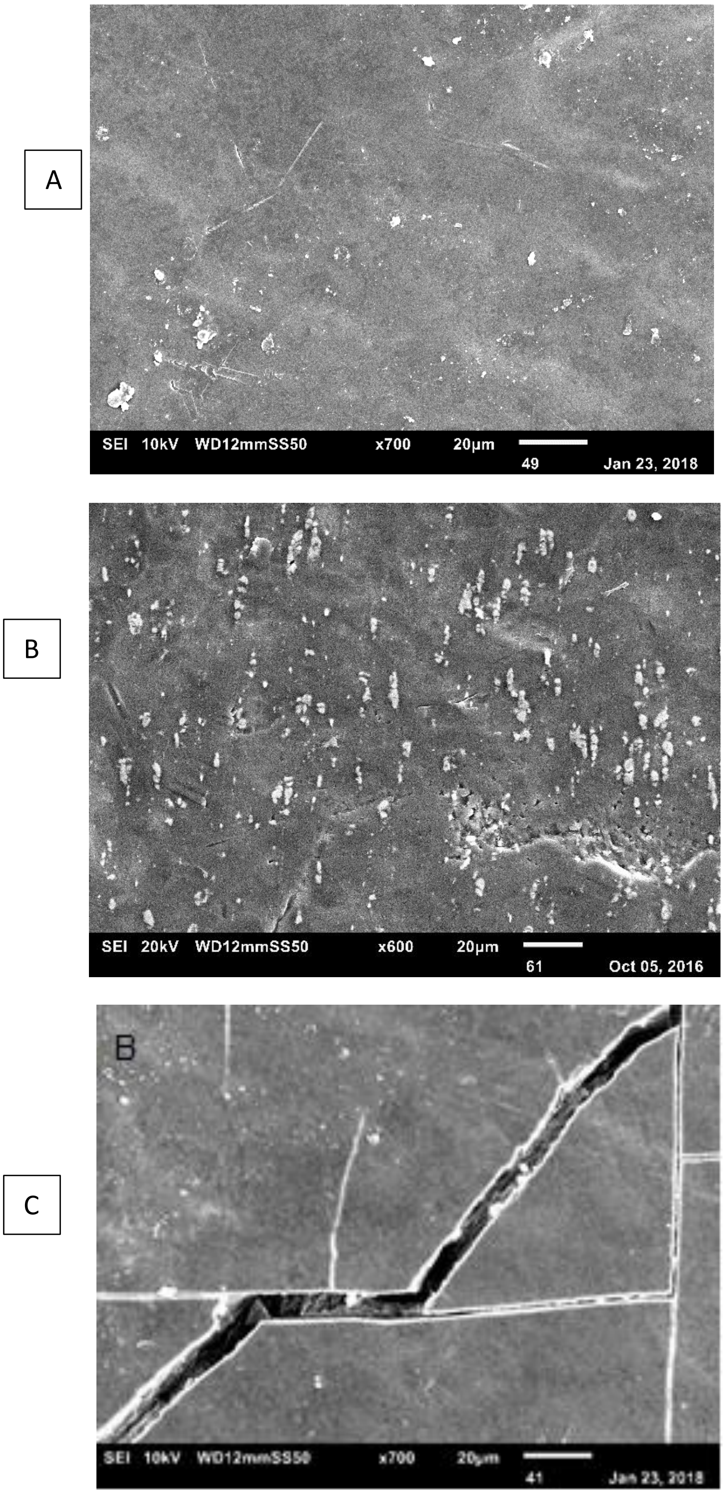

Figure 7.1: SEM micrographs (20µm) of DGEBA epoxy before (A) and after three (B), and six (C) months exposure to accelerated weathering

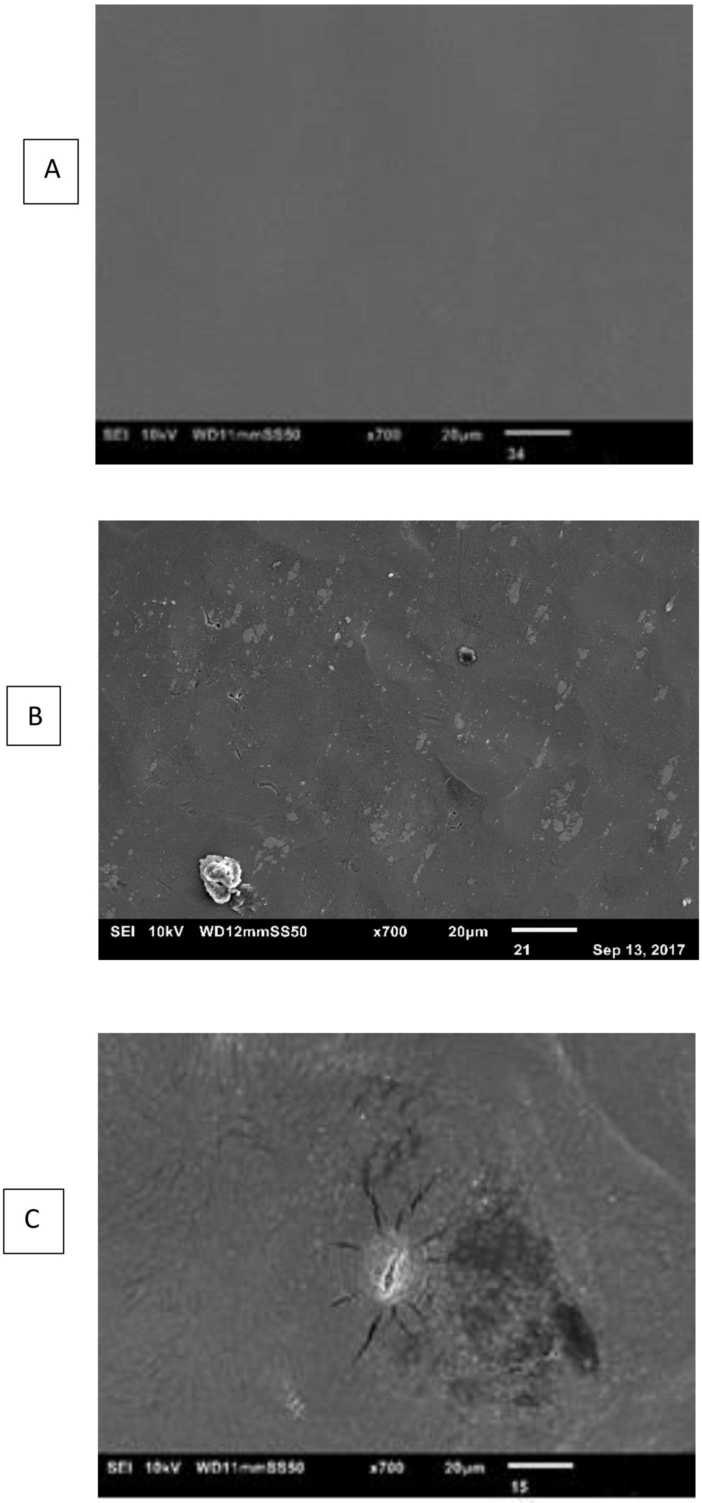

Figure 7.2: SEM micrographs (20µm) of HDGEBA before (A) and after three (B), and six (C) months exposure to accelerated weathering

7.2 SEM Analysis of Epoxy Resins/MWCNT Composites

Micrographs of DGEBA /0.5% MWCNT composite samples before and after exposure to three and six months' accelerated weathering are shown in Figure 7.3. Before exposure, the unexposed epoxy nanocomposite (HDGEBA/0.5% MWCNT) sample showed a smooth surface, and no cracks were found on it (Figure 7.4A). Before exposure, the SEM micrograph of DGEBA/0.5% MWCNT showed a smooth surface with the presence of a number of agglomerates observed (Figure 7.3A). These figures show that the surfaces are rough, with micro-sized particles that may be due to MWCNT or curing agents. After three months' exposure to accelerated weathering, the DGEBA samples exhibited more voids on the surface, compared to the DGEBA/0.5% MWCNT sample (Figure 7.3B). The cross-section of micrographs showed various artifacts (white lines), which are displayed on the cut sample surface of some samples, as shown in Figures 7.3 A, B, and C.

After six months' accelerated weathering, DGEBA epoxy resin sample showed a lot of very obvious cracks on the surface (Figure 7.1C), compared to the DGEBA/0.5% MWCNT composite (Figure 7.3C), but they are not propagating as well.

Micrographs of HDGEBA/0.5% MWCNT samples before and after exposure to three- and six-months' accelerated weathering are shown in Figure 7.4. Before exposure, the particles from HDGEBA/0.5% MWCNT sample were shown to have a homogeneous distribution on the surface and over its cross-section; no cracks found on the surface. After three- and six-months' exposure, no obvious cracks or voids are displayed on the surface of composite samples (HDGEBA /0.5% MWCNT), as shown in Figures 7.4 B and C. In Figure 7.4 (B and C), the HDGEBA/0.5% MWCNT composite samples indicate that the bonds between (HDGEBA) and (MWCNT) have better interfacial interactions compared to HDGEBA, which had weak interfacial interaction after exposure. From the overall results of SEM micrographs, HDGEBA

/0.5% MWCNT samples showed no cracks on the surface compared to other samples after six months' exposure to accelerated weathering, this may be attributed to the highest crosslinking density of HDGEB/0.5% MWCNT enhanced the resistance to increase the cracks on the surface compared to those of other samples.

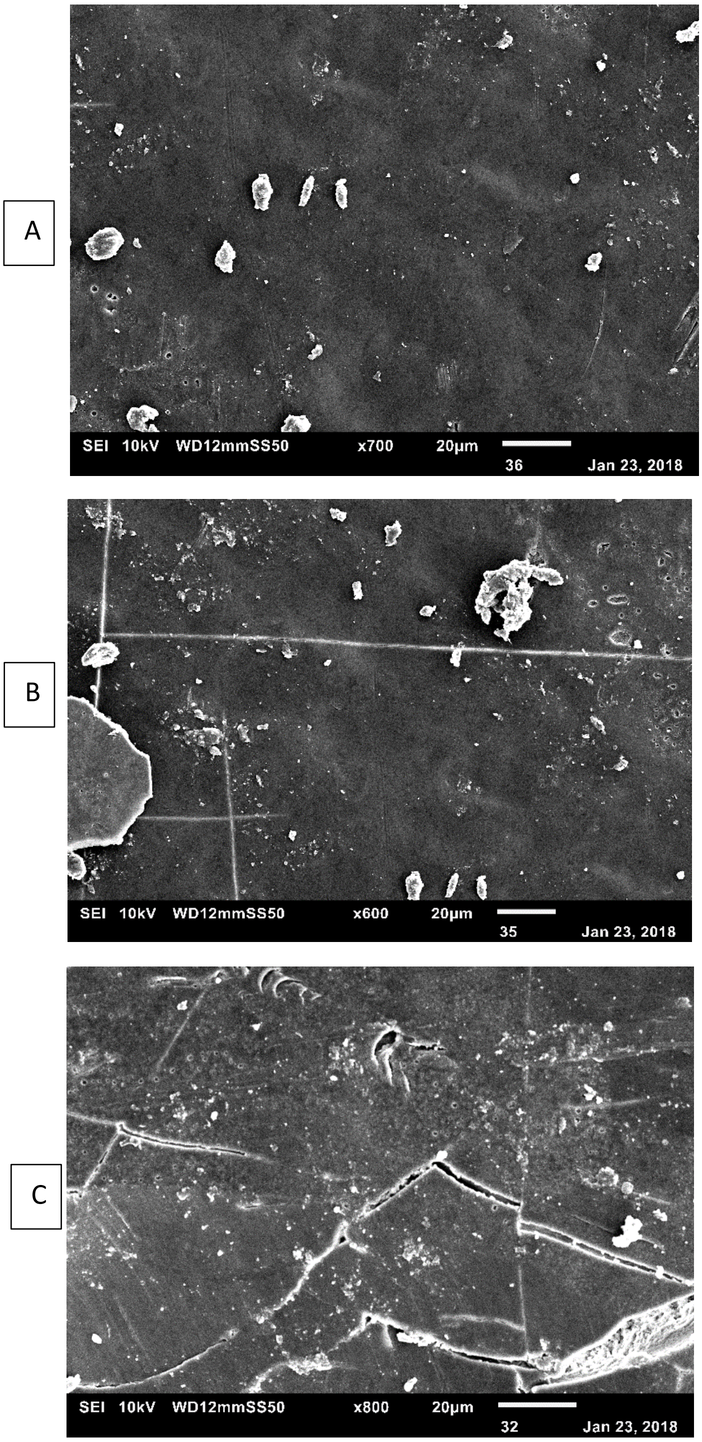

Figure 7.3: SEM micrographs (20µm) of DGEBA /0.5% MWCNT before (A) and after three (B), and six (C) months' exposure to accelerated

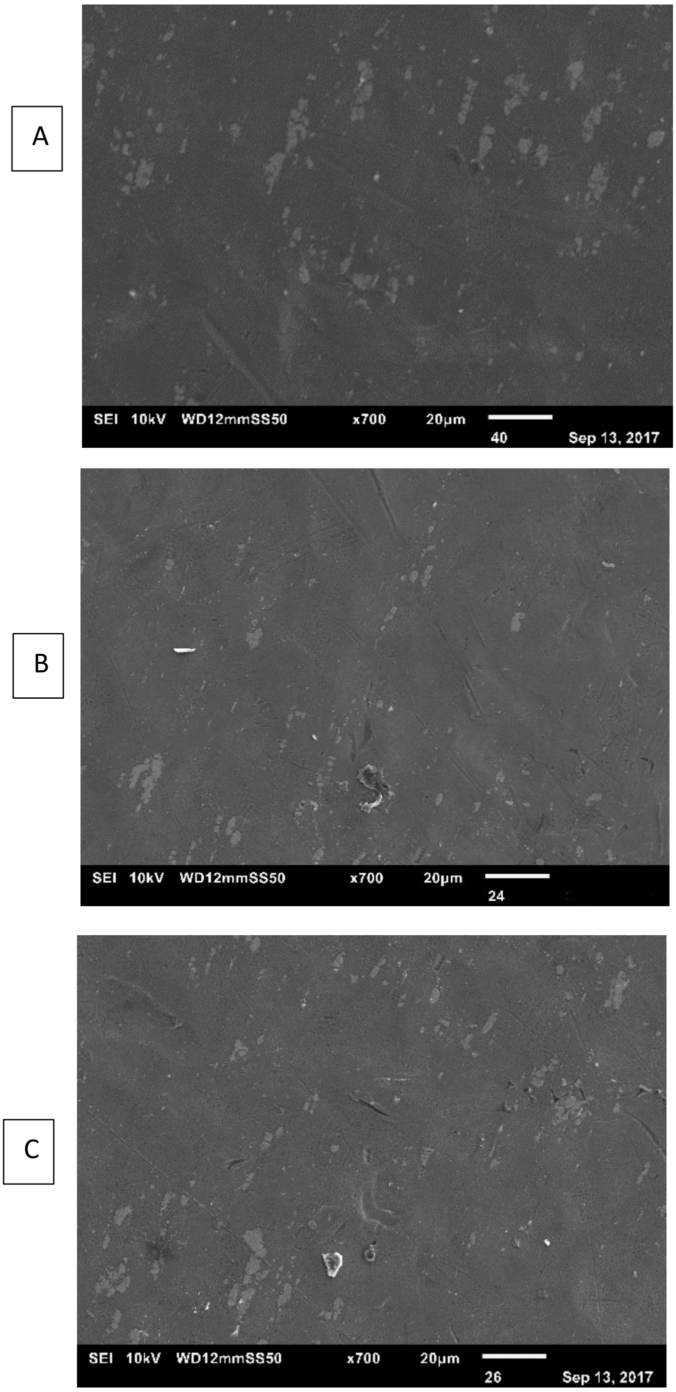

Figure 7.4: SEM micrographs of HDGEBA /0.5% MWCNT before (A) and after three (B) and, six (C) months' exposure to accelerated weathering

7.3 SEM Morphology of Epoxy Resins/CS Composites

The surfaces of DGEBA /2% CS and HDGEBA /2% CS composites before and after to three- and six-months' exposure to accelerated weathering are shown in Figures 7.5 and 7.6. Before exposure, the SEM micrographs of DGEBA/2% CS and HDGEBA /2% CS composite displayed no voids on the surface, as shown in Figures 7.5A and 7.6A. After six months of exposure to accelerated weathering, the surface of DGEBA/2% CS composite showed small cracks on it compared to the HDGEBA /2% CS composite (Figure 7.5C) [304]. The 2% CS in epoxy resins exhibited a smooth surface and fewer voids after exposure to three- and six-months' exposure compared to those of other epoxy composites, the reason is due to the high crystallinity of CS has a higher distribution into the epoxy matrix, hence enhances the crosslink density.

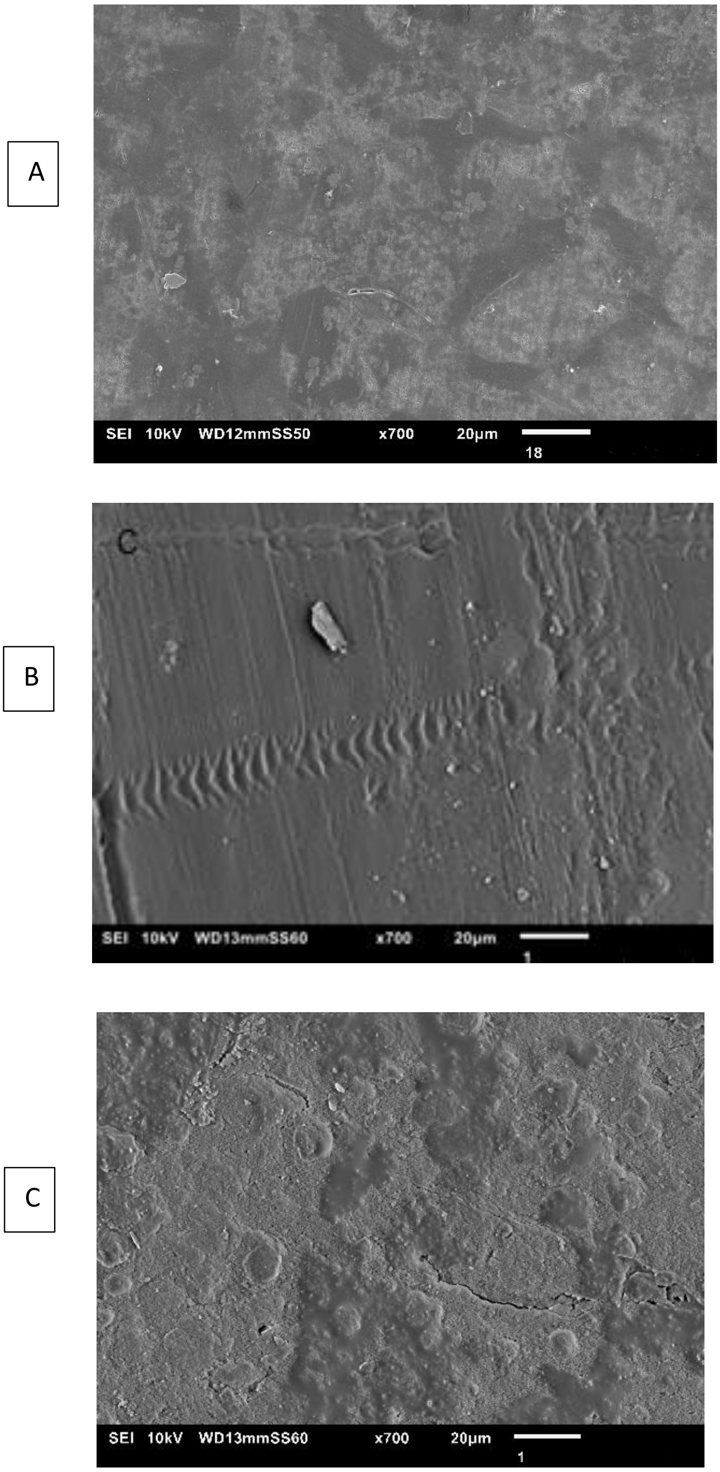

Figure 7.5: SEM micrographs of DGEBA /2% CS before (A) and after three (B), and six (C) months' exposure to accelerated weathering

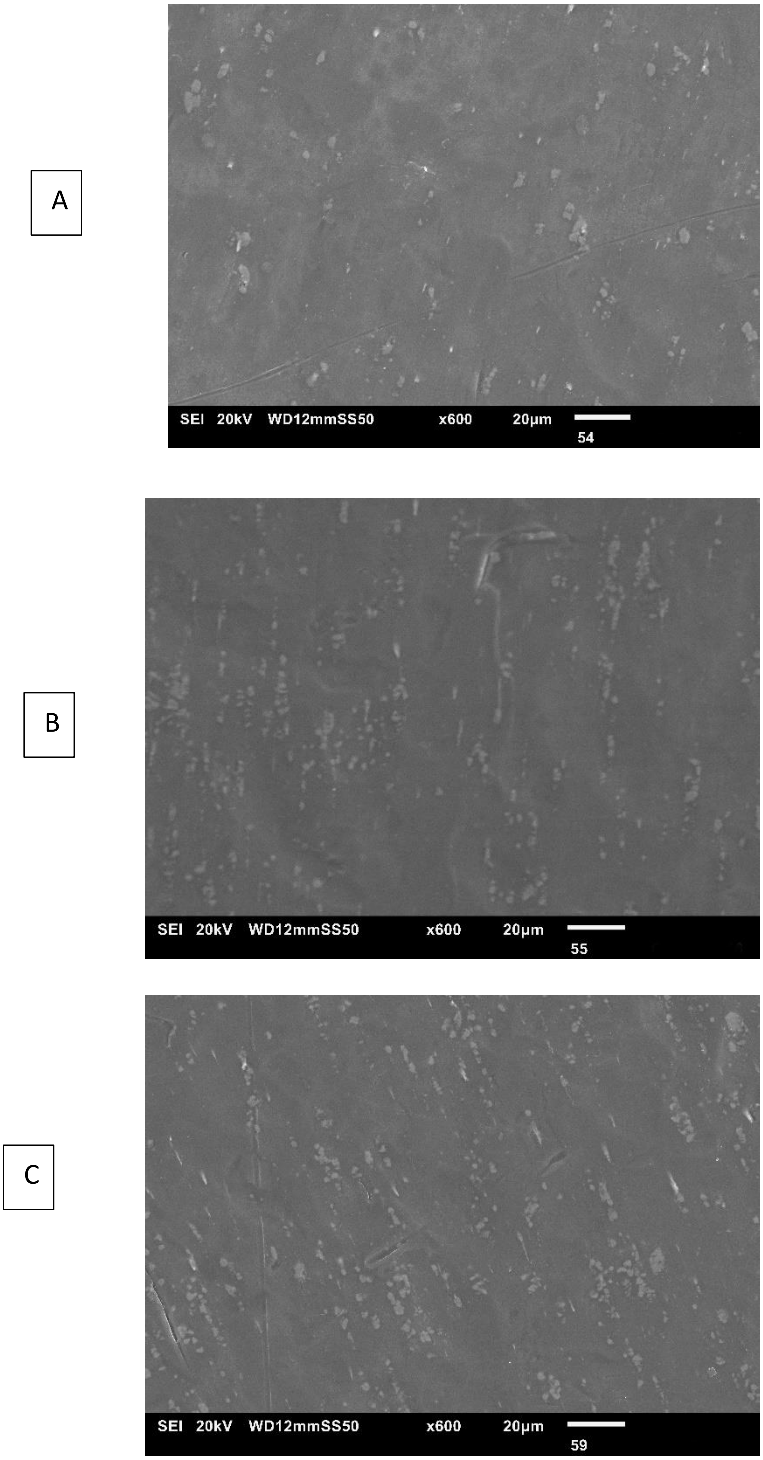

Figure 7.6: SEM micrographs of HDGEBA /2% CS before (A) and after three (B), and six (C) months exposure' to accelerated weathering

7.4 SEM Analysis of Epoxy Resins/MCC Composites

To study the effect of accelerated weathering on the surface morphology of epoxy samples, SEM micrograph was carried out on selected samples [306]. The surfaces of samples of DGEBA /2% MCC and HDGEBA/2% MCC composites before and after six months' exposure to accelerated weathering are shown in Figures 7.7 and 7.8, respectively. The surface of DGEBA/2% MCC sample showed limited voids after six months exposure to UV irradiation; after six months, the surface was covered with small voids as seen in Figure 7.7C. The surface of HDGEBA/2%MCC composite displayed limited voids on the surface (Figure 7.8C) after six months' exposure to accelerated weathering, compared to the surface of HGEBA/2% MCC composite before exposure to UV irradiation (Figure 7.8 A). It is possible that MCC domains, with different mechanical properties to the surrounding substrate, impede crack propagation, especially if they are plasticised with environmental water [322].

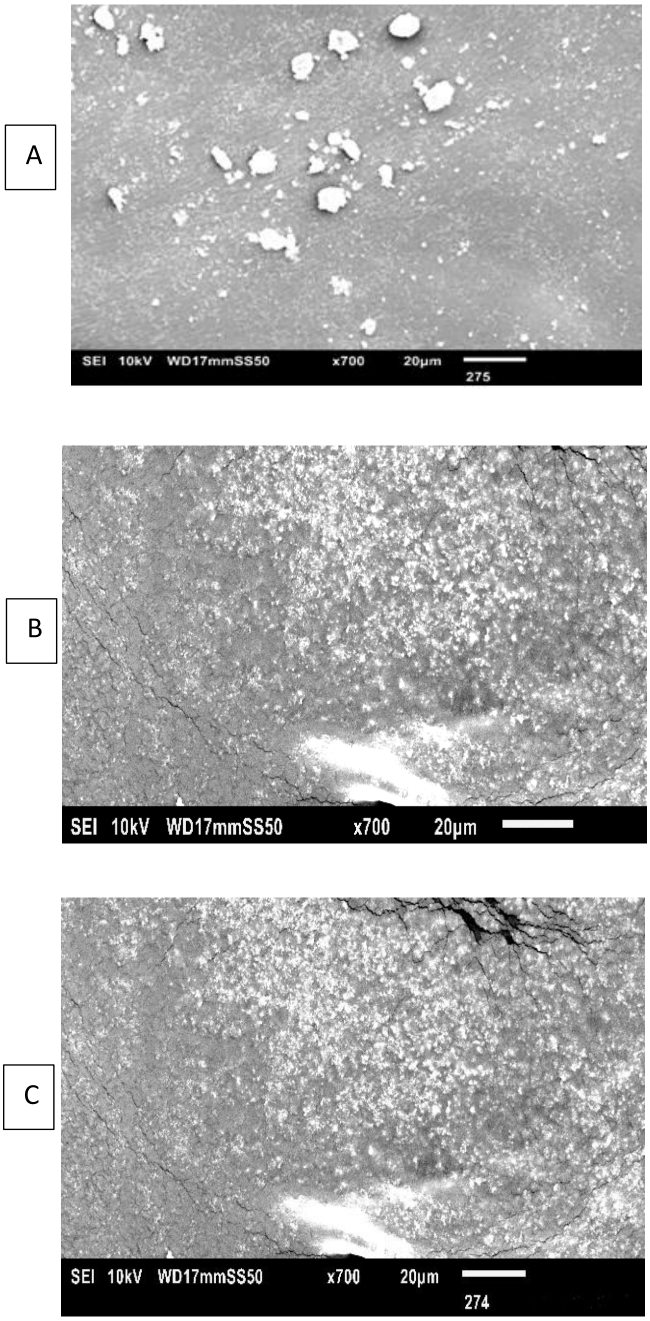

Figure 7.7: SEM micrographs of DGEBA /2% MCC before (A) and after three (B) and 6 (C) months' exposure to accelerated weathering

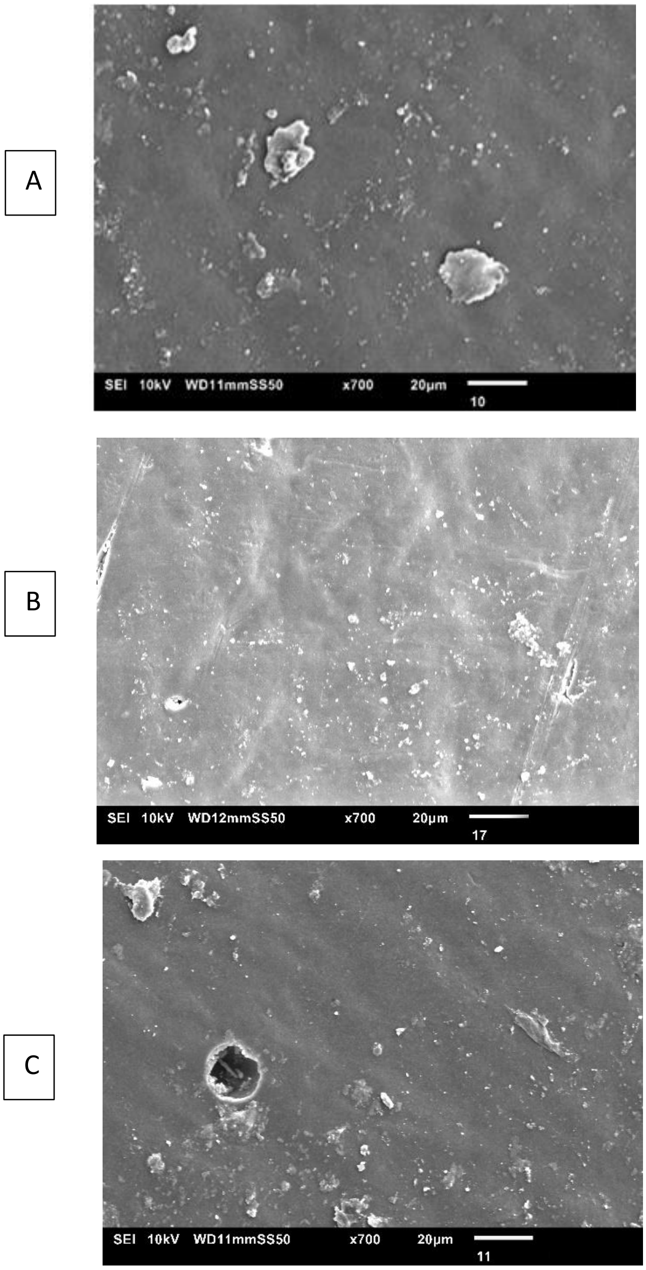

Figure 7.8: SEM micrographs of HDGEBA /2% MCC before (A), and after three (B) and six (C) months' exposure to accelerated weathering

7.5 General Discussion

Structural and surface changes of epoxy and epoxy composites were discussed in this chapter. The overall results of the morphology micrographs showed that the HDGEBA were more resistant to fracture on the surface than DGEBA and; all the changes on the surface that were showed in SEM micrographs are summarised in Table 7.1. Significant cracks were observed on the DGEBA surface six months' exposure compared to the HDGEBA surface; the reason may be due to the bonding between the curing agent and epoxy (DGEBA), which had poor interaction for DGEBA and HDGEBA (Figures 7.1C and 7.2C).

The SEM micrographs for HDGEBA composites showed less effect because of exposure to long-time accelerated weathering compared to that of DGEBA composites. The surface of HDGEBA/2% CS and HDGEBA/0.5% MWCNT displayed the highest resistance to reduction in the size of fractures on the surface compared to corresponding DGEBA composites. In the HDGEBA/2% CS and HDGEBA/0.5% MWCNT composites, compared to HDGEBA /2% MCC, HDGEBA, DGEBA, and DGEBA composites, the interfaces between DGEBA epoxy and TMDA are not crosslinked enough to resist the effect of six months' exposure to accelerated weathering compared to the surface of HDGEBA-TMDA, as shown in Figure 7.1(C) and 7.2 (C), respectively. From the overall results of SEM micrographs of DGEBA composites and HDGEBA composites, the CS into HDGEBA epoxy seems to be more effective at preventing the cracks on the DGEBA surface. The rough surface and cracks of DGEBA and DGEBA composites were found as a result of the poor adhesion between the epoxy matrix and fillers compared to those of the HDGEBA and HDGEBA composites. The results obtained from the SEM micrographs showed that with the addition of 2% MCC to epoxy resins, there were some cracks on the surface, which was also rougher after longer exposure (six months); this may be due to the brittle deformation and low resistance for crack propagation, resulting in low strength compared to that of epoxy incorporation CS and MWCNT. After six months' exposure, the HDGEBA/2% CS and HDGEBA/0.5% MWCNT composites did not show any cracks but had some small dents on the surface compared to those of other samples (SEM micrographs of DGEBA, HDGEBA and DGEBA composites).

Table 7.1: Comparison of the surface changes (SEM results) of all sample before and after three and six months' exposure to accelerated weathering

Samples	Before exposure	Three months	Six months
DGEBA	Little dents	Cross-section cracks	Big cross cracks
HDGEBA	Smooth surface	Little voids	Some voids
DGEBA/0.5% MWCNT	Smooth surface	No changes	Little voids
HDGEBA/0.5% MWCNT	Smooth surface	No changes	Little dents
DGEBA/2% CS	Smooth surface	No changes	Little fracture
HDGEBA/2% CS	Smooth surface	Smooth surface	No fracture
DGEBA/2% MCC	Little dents	Little cross cracks	Little fractures
HDGEBA/2%MCC	Little dents	Smooth surface	Little fracture

Chapter 8: X-Ray Diffraction Analysis

The change of X-ray diffraction (XRD) is a powerful nondestructive technique for characterising crystalline polymeric and epoxy materials [323]. It provides useful information on the changes of structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. The intensity peaks from XRD provide detailed information about the structural changes of all epoxy and epoxy composites before and after exposure to different accelerated weathering times [324]. From X-ray diffraction analysis, it is obvious that the increase of polarity in an epoxy resin, it is essential to reduce its area of cross-section, number of carbon atoms, the stiffness parameter, the particle size and the electron density fluctuations of amorphous epoxy resins. The presence of nitrogen atoms (N) of curing agent plays an important role in making an epoxy resin to be more insulators, and the outdoor weathering conditions may be caused changes of structural interaction of cured epoxy resins. This also concludes that the application of X-ray diffraction measurements leads to the successful interpretation of the structure of epoxy resins in terms of the presence of MWCNTs, CS, and MCC as stabilisers in their structure and to investigate the improvements in the chemical interaction. In this work, the XRD technique was used to evaluate the efficiency of modified epoxy resins and epoxy composites and is displaying more information regarding the structural changes in epoxy and epoxy composites before and after exposure to accelerated weathering [325-327].

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8.1 XRD of Epoxy Resins and Epoxy Composites

The XRD diffractograms of epoxy resins and epoxy composites were reported in Figures 8.1-8.8. It was possible to observe that all epoxy resins and epoxy composites reinforced with 0.5% MWCNT, 2% MCC, and 2% CS fillers after exposure to six months had slightly reduced of intensity peak comparing with those of all corresponding samples before exposure to accelerated weathering.

In case of the epoxy resins, from Figure 8.1, it was shown that the DGEBA before exposure shifted to be a higher intensity in comparison to the same sample after exposure of six months. The structure was also characterised by the presence of DGEBA, and HDGEBA epoxy resins in the presence of a peak at 19.35º and MWCNT was identified by an intense peak at 12.3º, and the wide diffraction (2θ) range (10º to 28º) is caused by scattering of the cured epoxy molecules, which reveals its amorphous nature. Note that all epoxy composites filled with 0.5% MWCNT, 2%CS, and 2%MCC fillers displayed similar diffraction patterns as the neat epoxy range. Before and after exposure to six months, the broad diffraction peaks appeared are shown in 2θ=19.5, and 45θ for Figures 8.1 and 8.2 are caused by the scattering of cured epoxy network and revealing its amorphous nature [325]. Before exposure, the intensity peaks (2θ=19.5º and 45 º) of DGEBA and HDGEBA were lower than those of the same epoxy resins after exposure to six months, as shown in Figures 8.1 and 8.2.

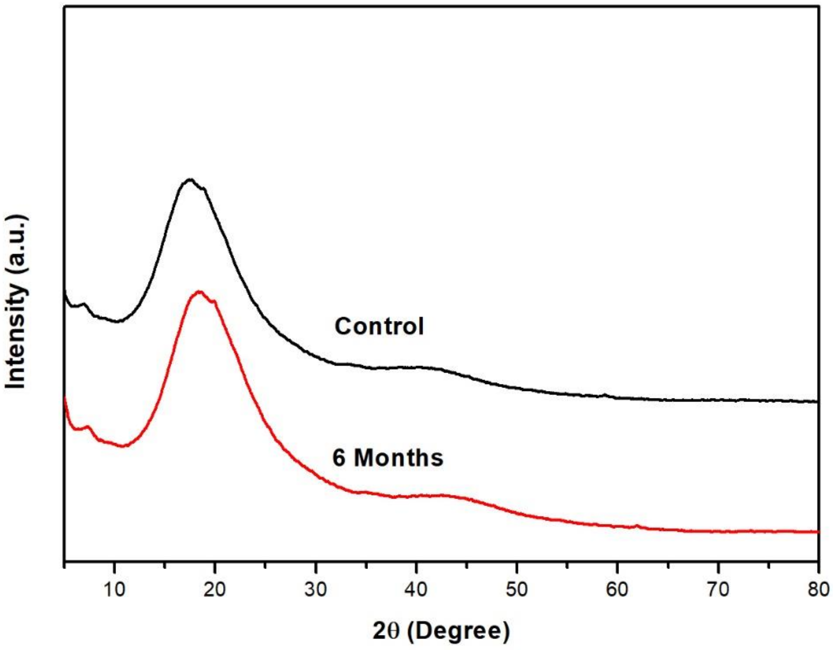

Figure 8.1: XRD spectra of DGEBA epoxy before and after exposure to six months accelerated weathering

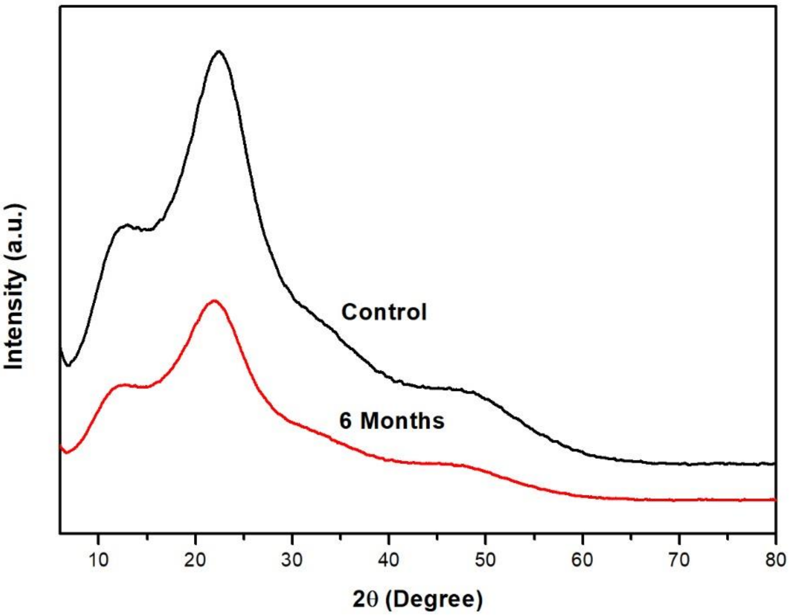

Figure 8.2: XRD spectra of HDGEBA epoxy before and after exposure to six months accelerated weathering

The diffraction peak of MWCNT was observed that the acid functionalisation had a significant influence on DGEBA peak width and intensity and the XRD peak of COOH-MWCNT in epoxy was at $2\theta = 7.5^{\circ}$. From Figure 8.3, the broad peaks at 2θ values 21.5° and 30.5°are due to the scattering from a cross-linked network of DGEBA epoxy, which indicates the amorphous nature of epoxy [326].

The intensity of DGEBA/0.5% MWCNT composite reduced after exposure to six months compared to that of the corresponding epoxy composite. There is a significant shift in the position of peaks of DGEBA/0.5% MWCNT ($2\theta = 21.5^{\circ}$), compared to that of DGEBA ($2\theta = 18.2^{\circ}$). This is due to the formation between the MWCNT and epoxy resin. The sharp peak at $2\theta = 30^{\circ}$ in DGEBA/0.5% MWCNT composite samples before and after exposure to six months accelerated weathering indicated to the reflection of inner with a spacing ($d = 3.346$ Å), which is slightly lower than the inter-planar spacing of epoxy incorporated with DGEBA, as shown in Figures 8.2 and 8.3. The HDGEBA /0.5% MWCNT composite displayed a higher reduction in the intensity peak compared to that of HDGEBA epoxy. The HDGEBA/0.5% MWCNT showed more shifted to the epoxy intensity peak ($2\theta = 20.5^{\circ}$) than the HDGEBA epoxy intensity peak.

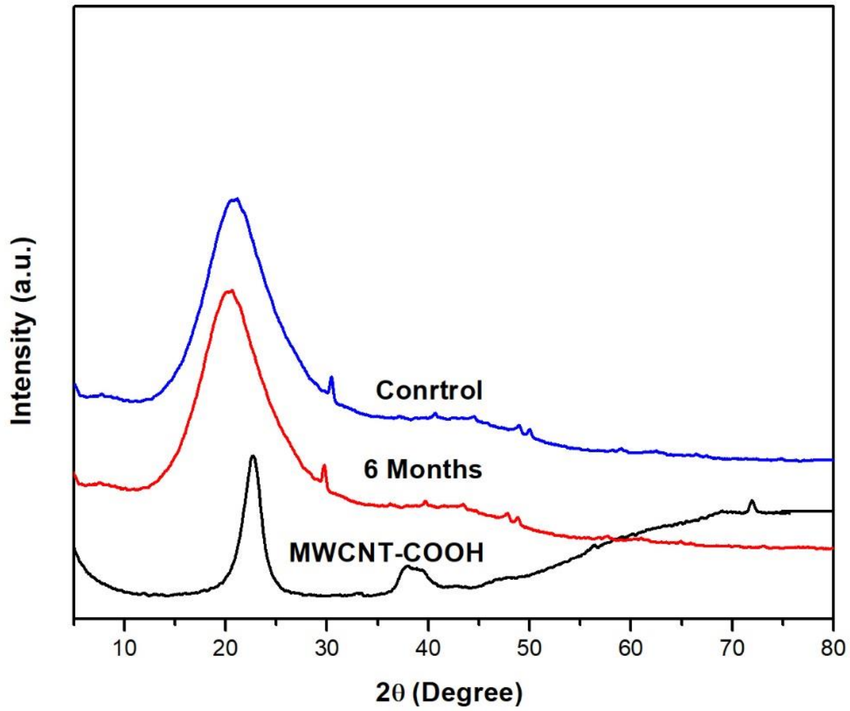

Figure 8.3: XRD spectra of DGEBA / 0.5% MWCNT composite samples before and after exposure to six months accelerated weathering

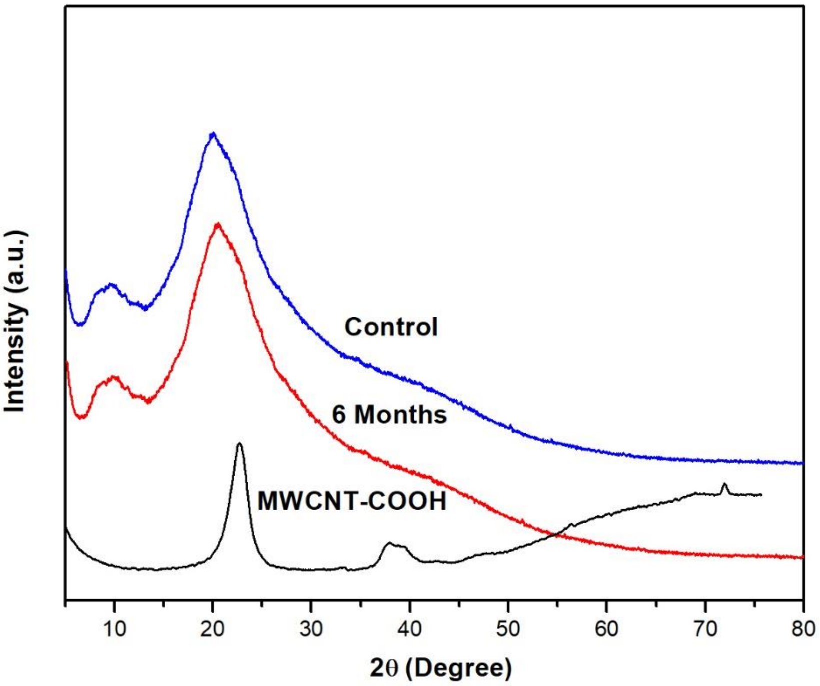

Figure 8.4: XRD spectra of HDGEBA / 0.5% MWCNT composite samples before and after exposure to six months accelerated weathering

In all the diffractograms, the peaks are observed at 2θ =16°, 22.5°, and 34.5°, corresponding to the microcrystalline cellulose (MCC) structure (Figures 8.5 and 8.6). The XRD pattern curves of DGEBA/2% MCC composites before and after exposure to six months accelerated weathering are shown in Figure 8.5. A reduction in intensity mainly in the major characteristic peak at 2θ =22.5º for MCC filler can be observed for both accelerated weathered composites and the decline is found to be greater for DGEBA composite than that for HDGEBA composite. This would be expected to be due to increased the degradation of the DGEBA composite during the accelerated weathering was confirmed with the mechanical and thermal properties of the accelerated weathered composites as discussed above (Figure 8.6).

From Figure 8.5, it was evident that there was no diffraction peak observed for the MCC-incorporated DGEBA system. A broad and disperse peak showed at 2θ =21.5 indicated the homogeneous and amorphous nature of resulting of DGEBA/MCC composite.

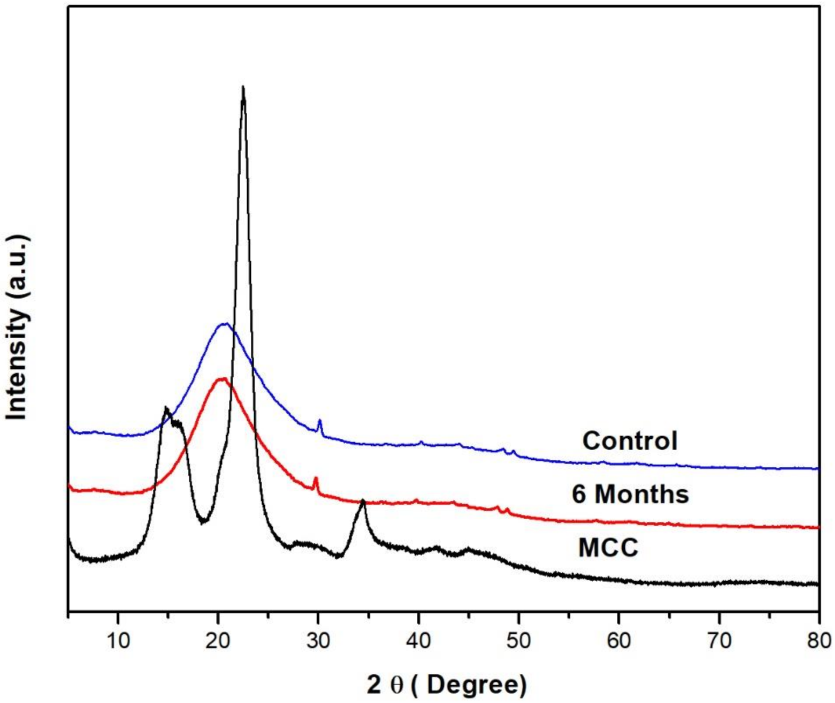

Figure 8.5: XRD spectra of DGEBA / 2% MCC epoxy before and after exposure to six months accelerated weathering

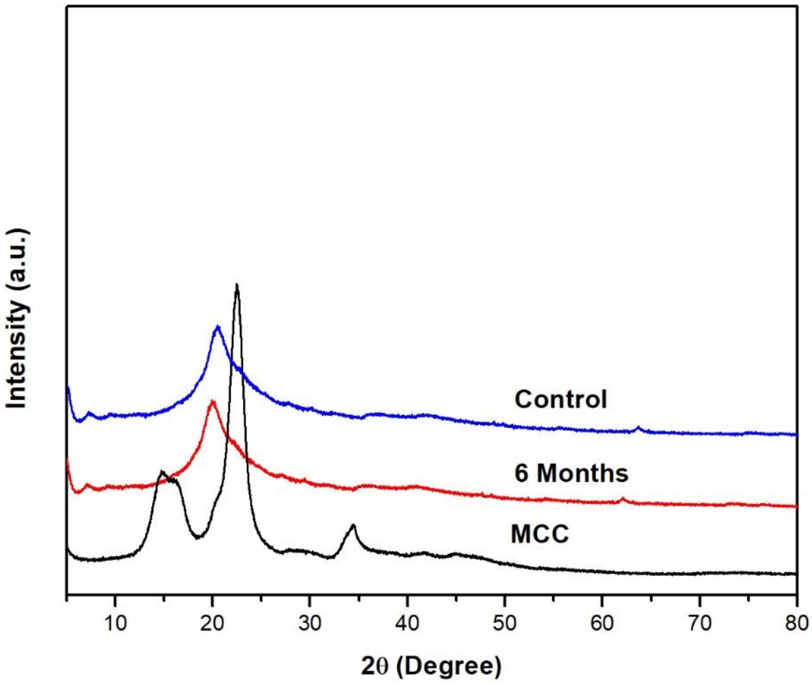

Figure 8.6: XRD spectra of HDGEBA / 2% MCC epoxy before and after exposure to six months accelerated weathering

The diffraction of XRD spectra in Figures 8.7 and 8.8 of DGEBA/2% CS and HDGEBA/2% CS, before exposure the spacing multi-peaks of CS almost disappeared, referring that the CS filer was exfoliated during the mixing. The intensity at 2θ=22.5º in a broad peak that is due to the HDGEBA epoxy resin. Some small intensity peaks were shown in Figures 8.7 and 8.8, which is due to the CS filler in epoxy resins. Before exposure, the XRD patterns of DGEBA/2% CS and HDGEBA/2% CS composites (38.5º, 44.5º, 47.6º, and 48.8º) also displayed small diffraction peaks that did not appear any significant changes after exposure of six months, which indicate that the synthesis of CS reinforced epoxy composites were a presence in high crystal quality.

The results obtained referred that HDGEBA sample had a higher intensity compared to that of the corresponding sample after exposure to six months exposure with a higher shift of the intensity peak. With the similarity of the intensity peaks of HDGEBA/2% CS, DGEBA/2% CS samples after six months of exposure, the intensity peaks were reduced with lesser shift toward the intensity peaks of epoxy (2θ = 26.2°) compared to that of HDGEBA/2% CS. Both of DGEBA/2%CS and HDGEBA /2% CS showed a decrease in intensity after exposure of six months in comparison to the same samples before exposure. This may be as results to the exposure to accelerated weathering to six months and caused a reduction in the crystallinity (Figures 8.7 and 8.8).

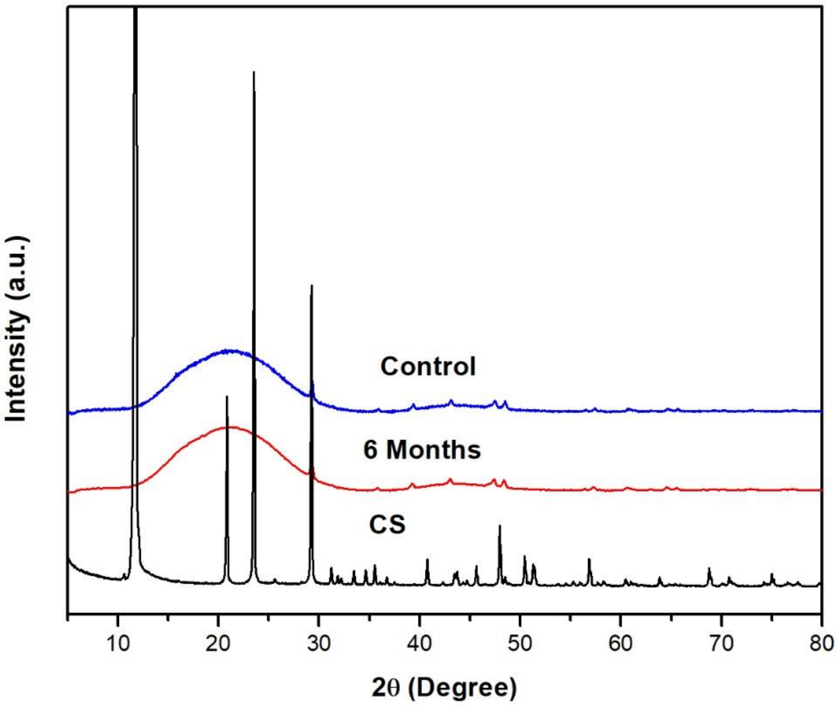

Figure 8.7: XRD spectra of DGEBA / 2% CS composite samples before and after exposure to six months accelerated weathering

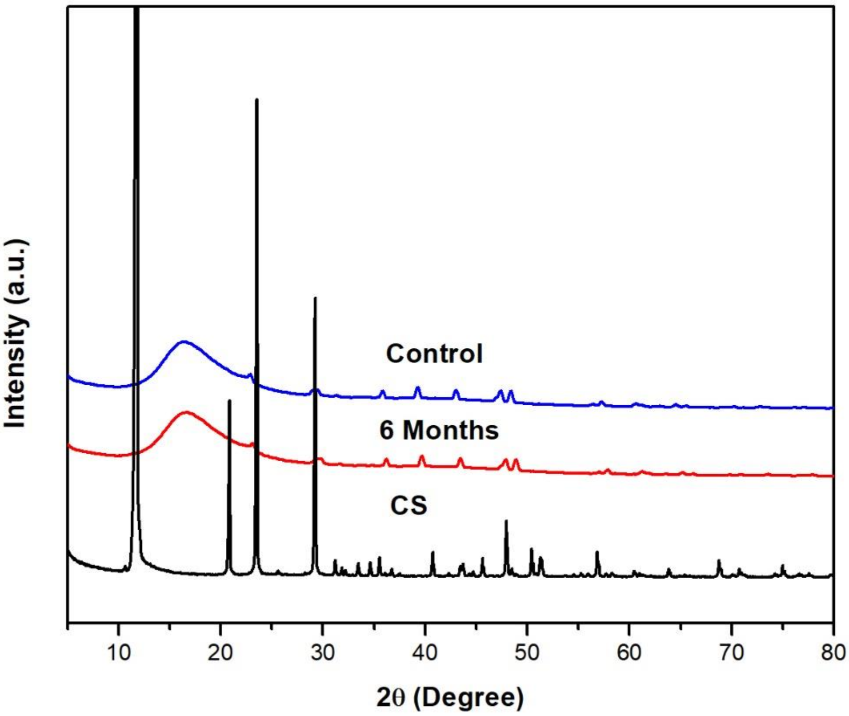

Figure 8.8: XRD spectra of HDGEBA / 2% CS composite samples before and after exposure to six months accelerated weathering

8.2 General Discussion

The XRD patterns of epoxy and epoxy composites were investigated to analysis the reductions in the intensity peaks of epoxy resins after filled with different fillers, and after exposure to six months accelerated weathering and determine the presence of homogeneous distribution of fillers in the epoxy composites. The broad diffraction peaks from 5° to 28° is caused by scattering of the cured epoxy molecules, revealing its amorphous nature [325]. A broad amorphous peak observed at $2\theta = 5–28$ infers the complete dispersion of reinforcements in the TMDA blended epoxy matrix. All results obtained did not exhibit changes or shifts into the epoxy resins. However, the intensities of epoxy composites were reduced by comparing to those of two epoxy resins (DGEBA and HDGEBA). These the results obtained were proved based on many works [326,327]. They reported that epoxy composites show a peak in the diffractogram around $2\theta = 20^{\circ}$, which is quite analogous.

Furthermore, from the XRD plot, it is evident that the addition of MWCNT, MCC, CS fillers into the epoxy matrix does not result in any significant changes to its crystallinity. By the comparison of the investigation of the effect the intensity of epoxy resins and epoxy composites, using XRD analysis in this chapter, another previous work investigated the effect of accelerated weathering (UV irradiation and moisture conditions) on the intensity properties of DGEBA composites. They found that the intensity peak ($2\theta=22.5^{o}$) was decreased after exposure to 1000 h compared to that of the corresponding sample before exposure [327]. By briefly, at the accelerated weathering to up six months, the intensity was decreased of all epoxy and epoxy composites. The intensity of the peak is less in HDGEBA/CS when compared to the other epoxy composites, which may be due to the semi crystalline nature of CS into epoxy resins which increase the intensity of the peak [328,329]. XRD ascertain the presence of a homogeneous distribution of fillers in the epoxy composites. The XRD patterns of CS, MWCNT, and MCC fillers-reinforced DGEBA blend epoxy systems suggest the formation of intercalated nanohybrids due to a shift the diffraction peak towards the lowest angle [329].

Chapter 9: Conclusions and Recommendations for Future Research

9.1 Conclusions

The durability of epoxy resins are utilised in engineering timber composite applications was evaluated by exposure to artificial accelerated weathering. Based on the results of this work, it is concluded that the fillers used in formulation needs to be suited to different epoxy resins. The HDGEBA epoxy and HDGEBA composites displayed the best overall performance after exposure to six months accelerated weathering as following:

- The chemical degradation on the surface of epoxy and epoxy composites obtained from the results of ATR-FTIR experiments were evaluated by measuring the areas of carbonyl and hydroxyl bands (carbonyl and hydroxyl indices). The results showed that HDGEBA composites are more effective, more reduced to increase of carbonyl and hydroxyl indices in comparison with the DGEBA composites after exposure for a longer time (six months). However, the HDGEBA/2%CS and HDGEBA/0.5%MWCNT composites exhibited more reduction in increasing of the indices that may be due to the high interactions with epoxy radicals. Another reason may be due to the higher crystallinity of CS filler in the epoxy resin leading to oxygen starvation in the crystalline phase producing lower photodegradation.
- From the mechanical results, the tensile strength of HDGEBA composites showed less reduction than DGEBA composites after exposure for six months. The HDGEBA epoxy and HDGEBA composites showed a higher resistance to reduce the loss in tensile strength and the elongation at break after exposure to different accelerated weathering times. The results of DMA on the selected DGEBA and DGEBA/0.5% MWCNT

composites exhibited improvements in reducing mechanical degradation, which complies with others' research.

- The fillers (MWCNT and CS) in HDGEBA epoxy (aliphatic epoxy) were more effective than DGEBA composites in reducing the weight loss (TGA) and resistance to decrease the T_g values and the tensile strength.
- The T_g values from DSC curves showed that the HDGEBA/2% CS and HDGEBA/0.5%MWCNT are more effective in decreasing the loss in T_g than the HGEBA/2%MCC, DGEBA, and DGEBA composites. However, the T_g values before and after exposure to six months were higher than HDGEBA and HDGEBA composites.
- From SEM tests, HDGEBA composites exhibited great improvements of the surface degradation resistant after accelerated weathering of exposure and showed smooth surface and small cracks on the surface compared to those of DGEBA composites.
- The results of XRD showed that the intensity of all epoxy and epoxy composites was reduced by comparing the corresponding samples before exposure. The results of XRD were confirmed by the SEM results, which showed the HDGEBA composites exhibited less reduction in intensity than the DGEBA composites after six months' exposure.

9.2 Recommendations for Future work

Some recommendations of future research resulted from proposed research to provide more information about the significance of research are presented below:

One of the significant limitations of this investigation is the effect of accelerated weathering up to six months on the epoxy resins and epoxy composites and with a fixed concentration of fillers into epoxy resins. Perhaps using longer exposure time with different concentrations of fillers will be a greater significance to evaluate the epoxy properties after exposure to outdoor environmental conditions.

1. Extend the exposure times (UV irradiation and moisture exposure) to 12 months and investigate the impact of DGEBA and HDGEBA epoxies and their composites.
2. Use different concentrations of photostabilisers (nanoclay, organic stabilisers) as additives to epoxy resins and comparing the effects before and after exposure to 12 months accelerated weathering and evaluate its impacts by evaluating chemical, thermal, mechanical changes.
3. A comparison study ~~of~~ the effects of particle size of filler with different concentrations on the natural weathering with accelerated artificial weathering tester on the epoxy resins and epoxy composites.
4. Extraction of epoxy and epoxy composites before and after exposure to different accelerated weathering times and the extracted samples analyses by using NMR and GC-MS techniques in order to evaluate the chemical and structural changes during the exposure times.
5. The HDGEBA and HDGEBA/2% CS and HDGEBA/0.5%MWCNT are exhibited excellent resistant to accelerated weathering based on the results obtained from this work, and they can be recommended as a practical use to improve the durability of engineering timer composites.

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Appendix A

Part (A): Mechanical Tests

A.1. Chapter Overview

Continued in this appendix for results of the values for mechanical tests in Chapter 5 for all samples before and after exposure to different accelerated weathering times

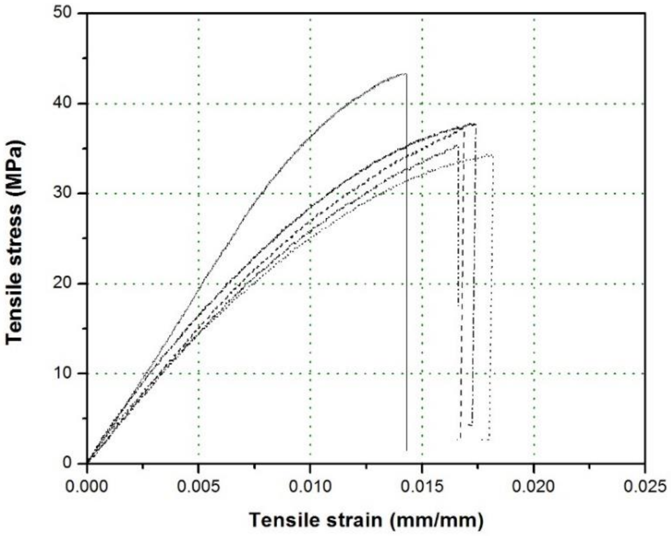


Figure A.1: Five replicate tensile stress-strain curves of DGEBA epoxy after one month exposure to accelerated weathering

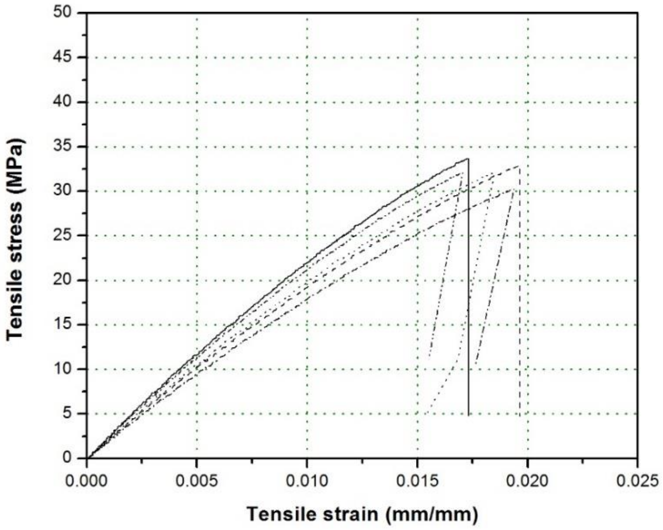


Figure A.2: Five replicate tensile stress-strain curves of DGEBA epoxy after two months exposure to accelerated weathering

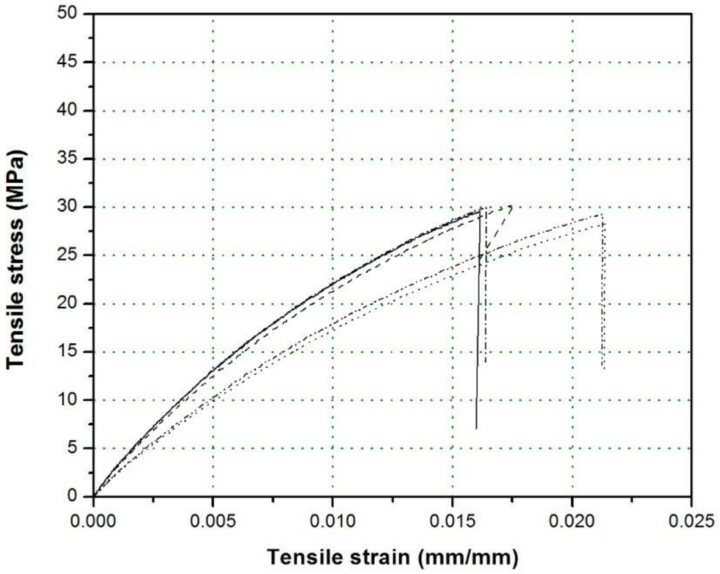


Figure A.3: Five replicate tensile stress-strain curves of DGEBA epoxy after three months exposure to accelerated weathering

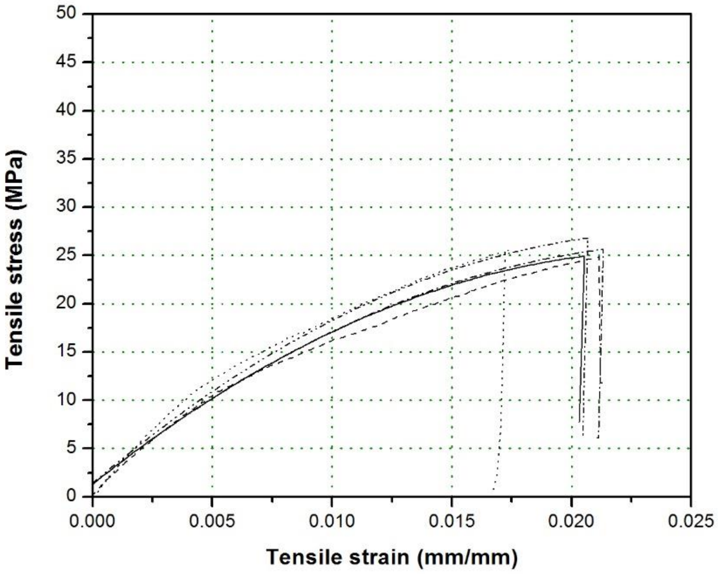


Figure A.4: Five replicate tensile stress-strain curves of DGEBA epoxy after four months exposure to accelerated weathering

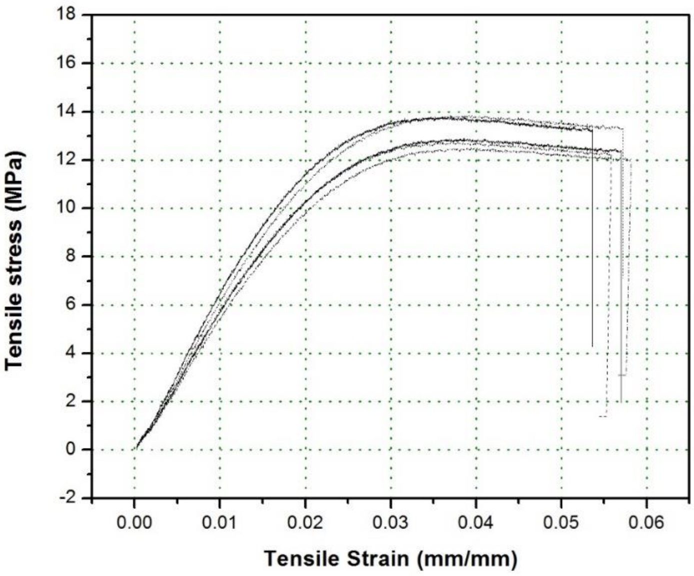


Figure A.5: Five replicate stress-strain curves of HDGEBA epoxy after one month exposure to accelerated weathering

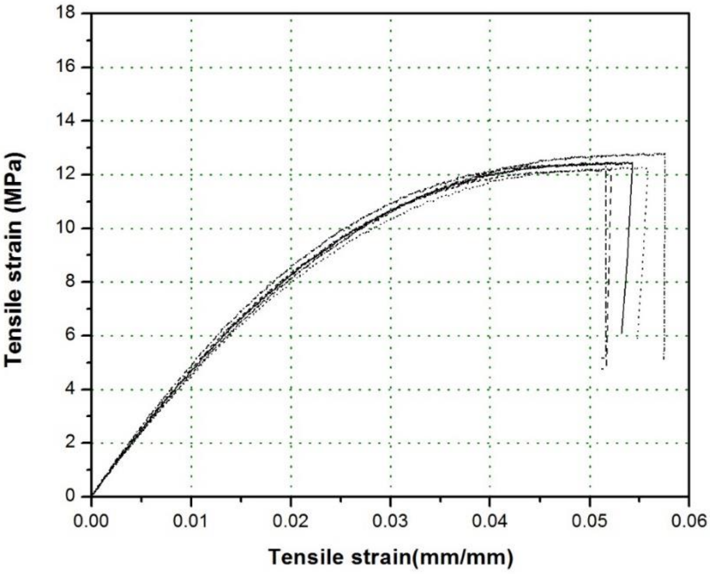


Figure A.6: Five replicate tensile stress-strain curves of HDGEBA epoxy after two months exposure to accelerated weathering

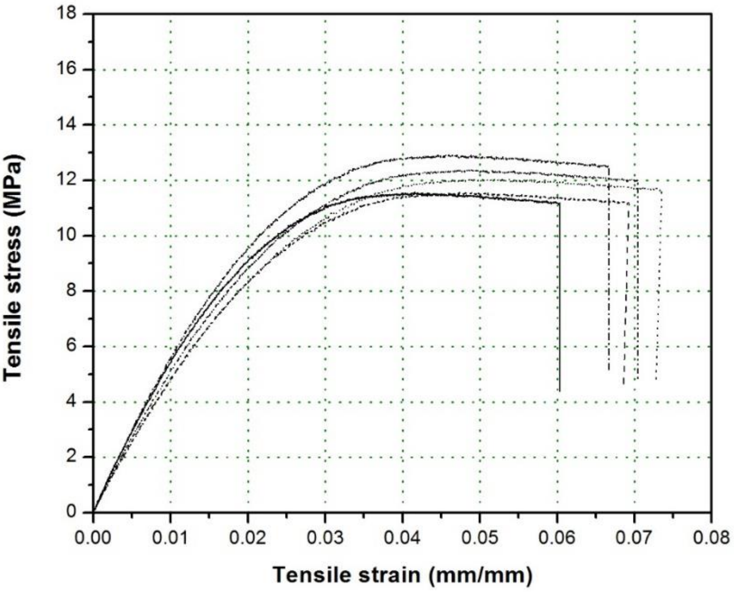


Figure A.7: Five replicate tensile stress-strain curves of HDGEBA epoxy after three months exposure to accelerated weathering

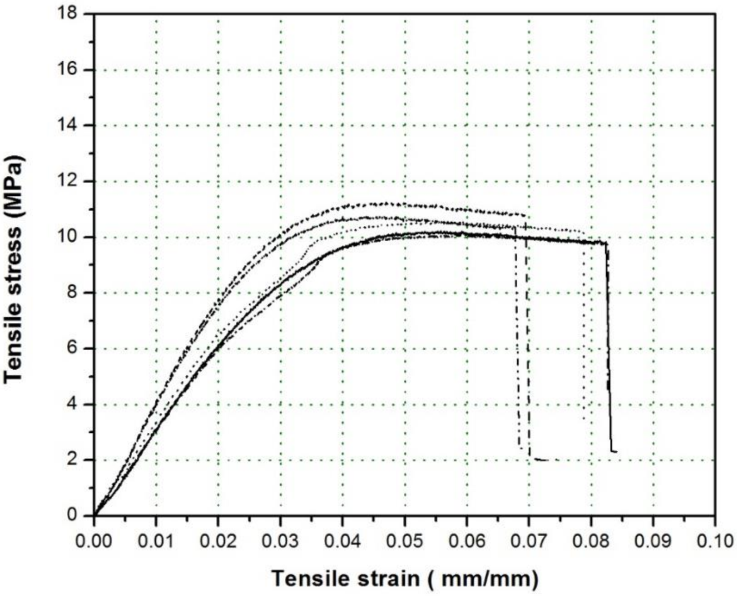


Figure A.8: Five replicate tensile stress-strain curves of HDGEBA epoxy after four months exposure to accelerated weathering

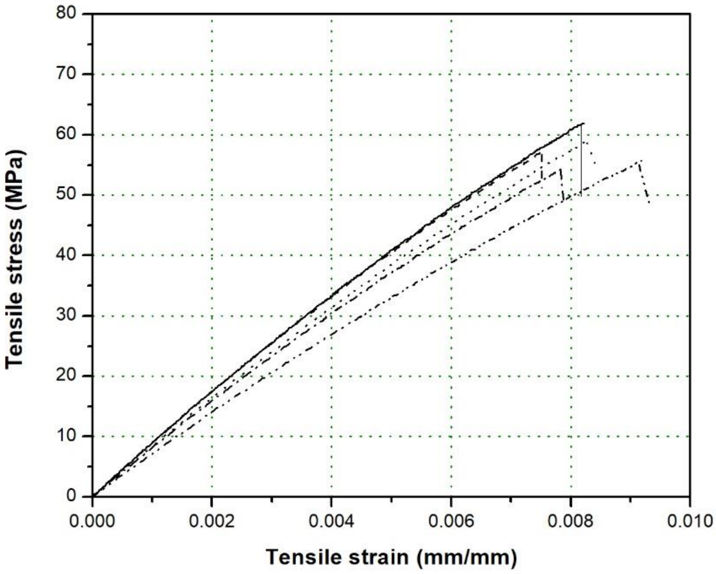


Figure A.9: Five replicate tensile stress -strain curves of DGEBA /0.5% MWCNT after one month exposure to accelerated weathering

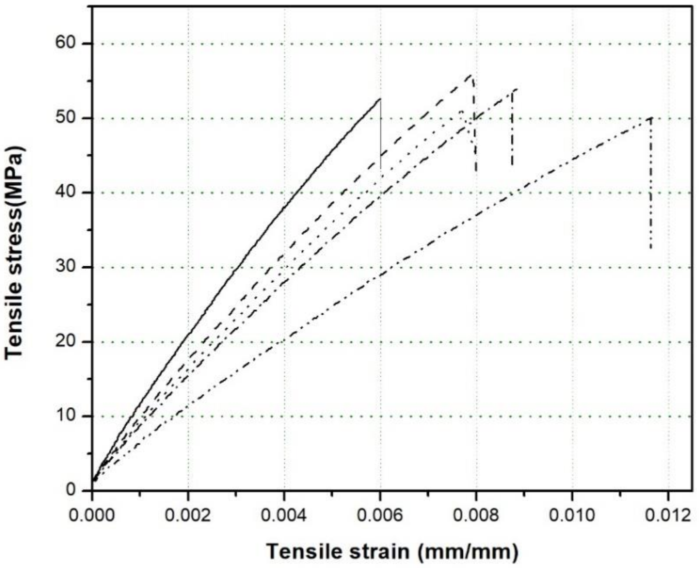


Figure A.10: Five replicate tensile stress -strain curves of DGEBA /0.5% MWCNT after two months exposure to accelerated weathering

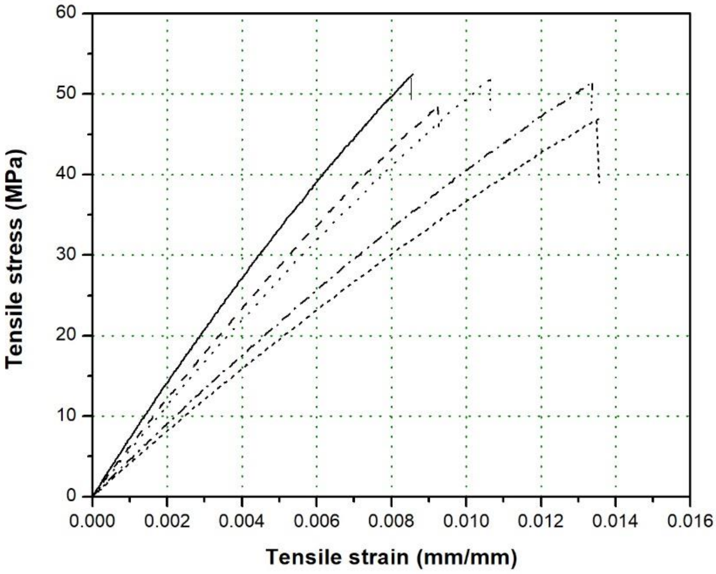


Figure A.11: Five replicate tensile stress -strain curves of DGEBA /0.5% MWCNT after three months of exposure to accelerated weathering

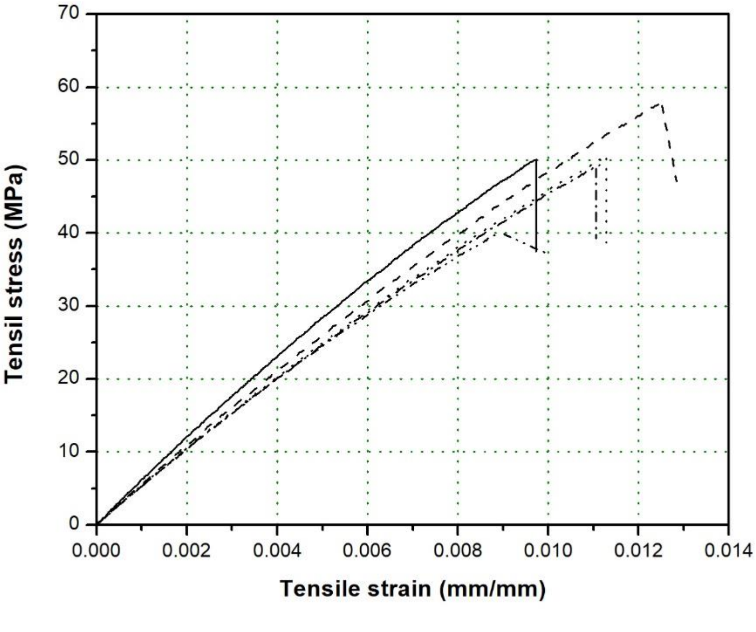


Figure A.12: Five replicate tensile stress -strain curves of DGEBA/0.5% MWCNT after four months of exposure to accelerated weathering

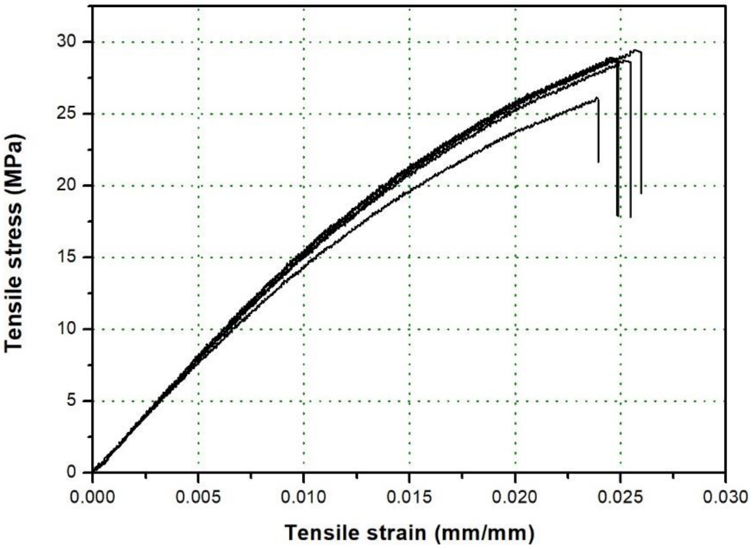
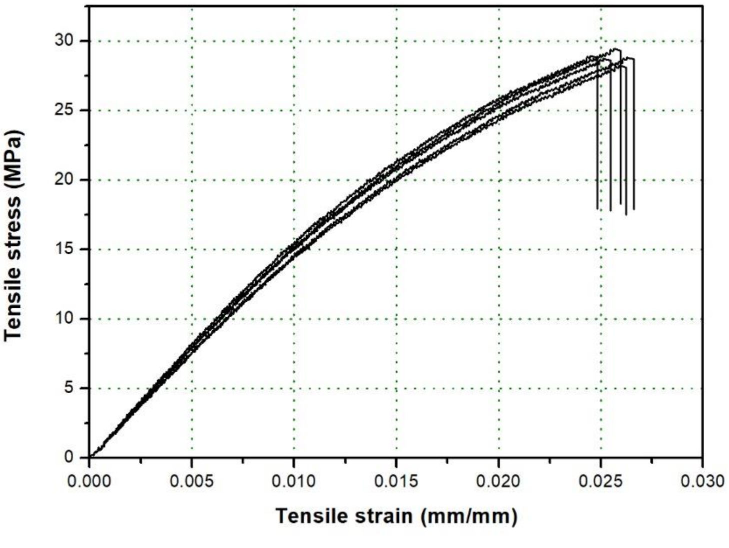


Figure A.13: Five replicate tensile stress -strain curves of HDGEBA /0.5% MWCNT after one month of exposure to accelerated weathering



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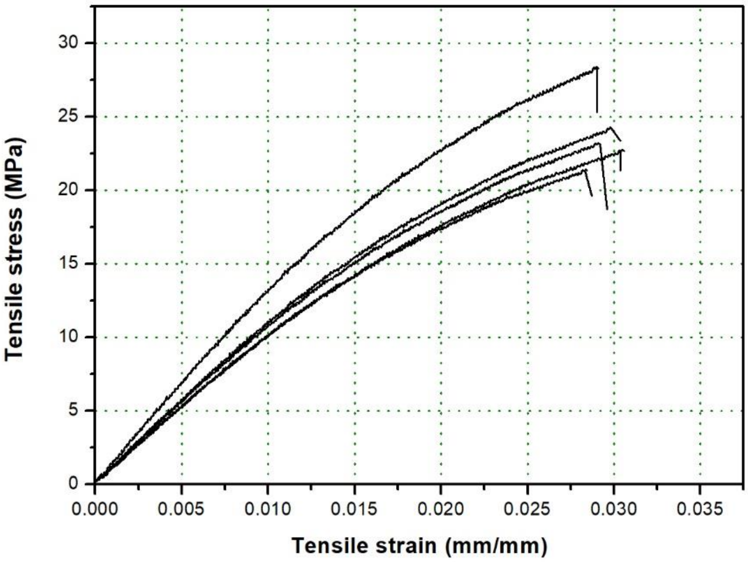

Figure A.15: Five replicate tensile stress -strain curves of HDGEBA /0.5% MWCNT after three months of exposure to accelerated weathering

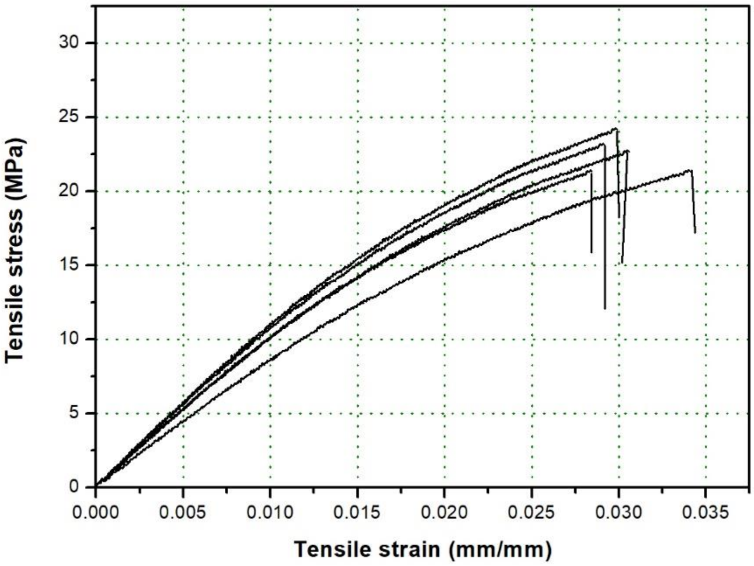

Figure A.16: Five replicate tensile stress -strain curves of HDGEBA /0.5% MWCNT after four months of exposure to accelerated weathering

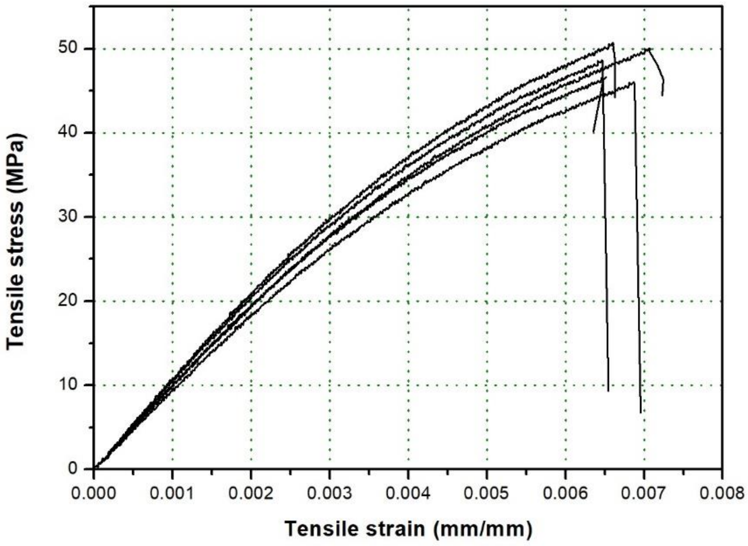

Figure A.17: Five replicate tensile stress -strain curves of DGEBA /2% MCC after one month of exposure to accelerated weathering

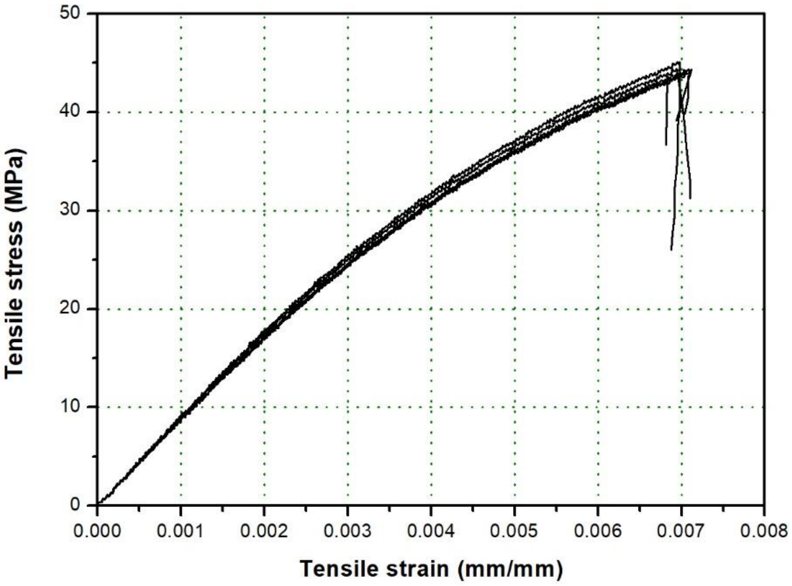

Figure A.18: Five replicate tensile stress -strain curves of DGEBA /2% MCC after two months of exposure to accelerated weathering

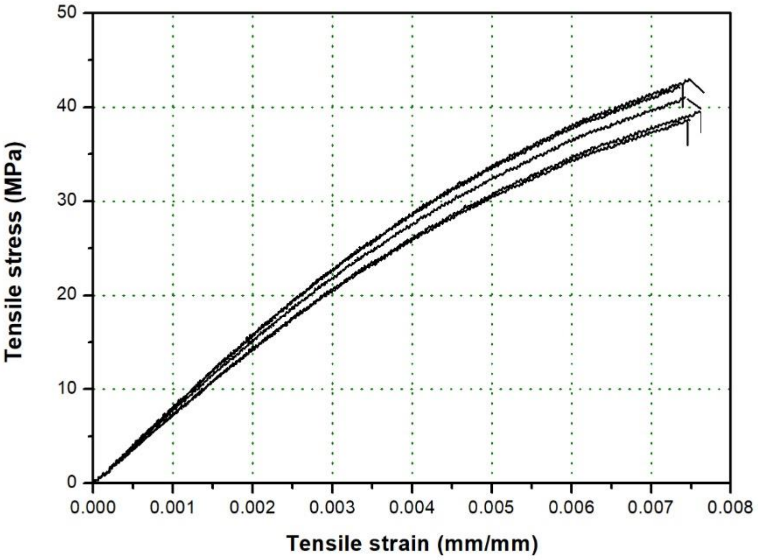

Figure A.19: Five replicate tensile stress -strain curves of DGEBA /2% MCC after three months of exposure to accelerated weathering

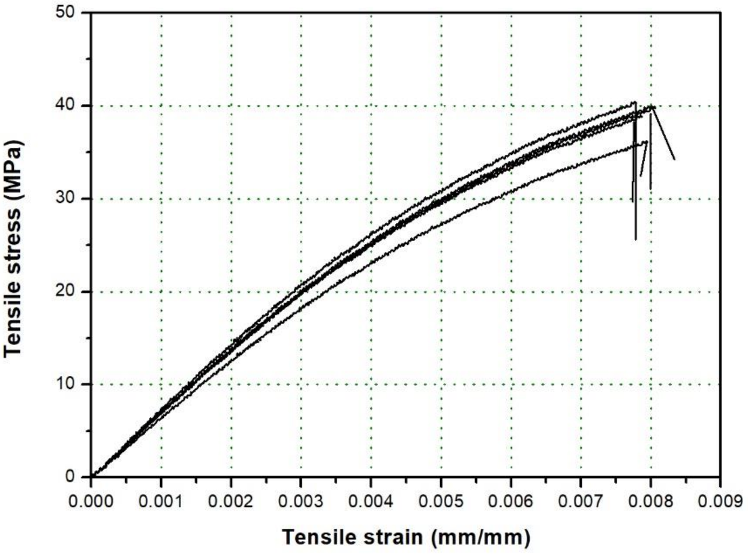

Figure A.20: Five replicate tensile stress -strain curves of DGEBA /2% MCC after four months of exposure to accelerated weathering

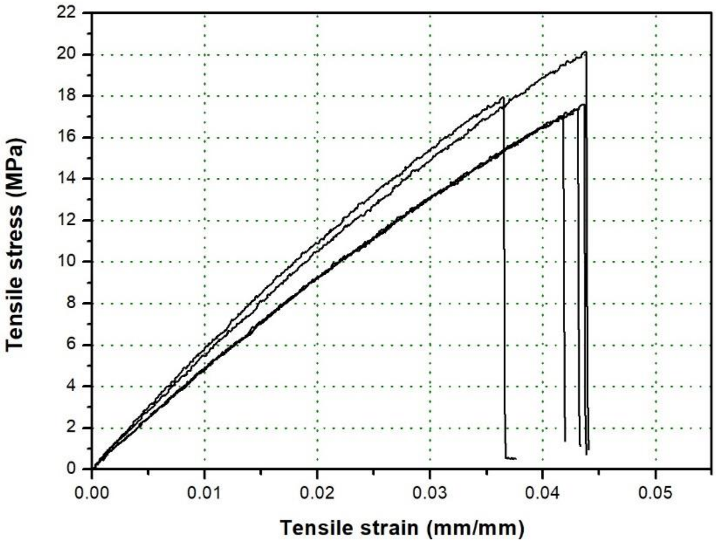

Figure A.21: Five replicate tensile stress -strain curves of HDGEBA /2%MCC after one month of exposure to accelerated weathering

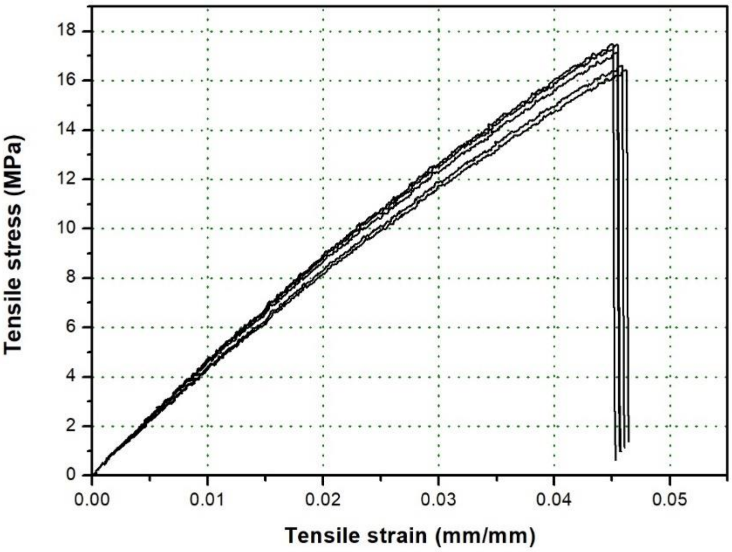

Figure A. 22: Five replicate tensile stress -strain cuves of HDGEBA /2% MCC after two months of exposure to accelerated weathering

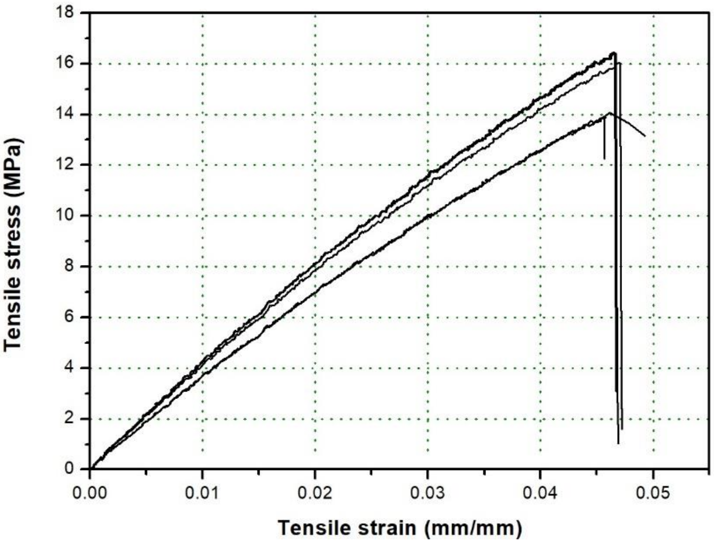

Figure A.23: Five replicate tensile stress -strain curves of HDGEBA /2% MCC after three months of exposure to accelerated weathering

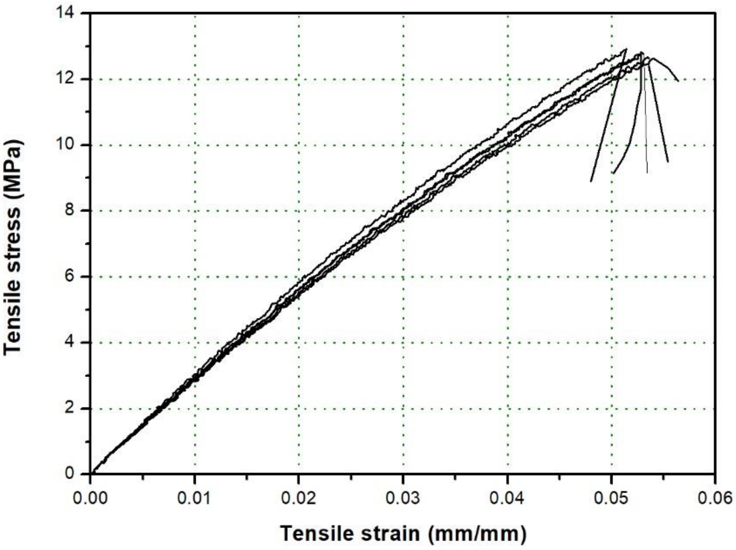

Figure A.24: Five replicate tensile stress -strain curves of HDGEBA /2% MCC after four months of exposure to accelerated weathering

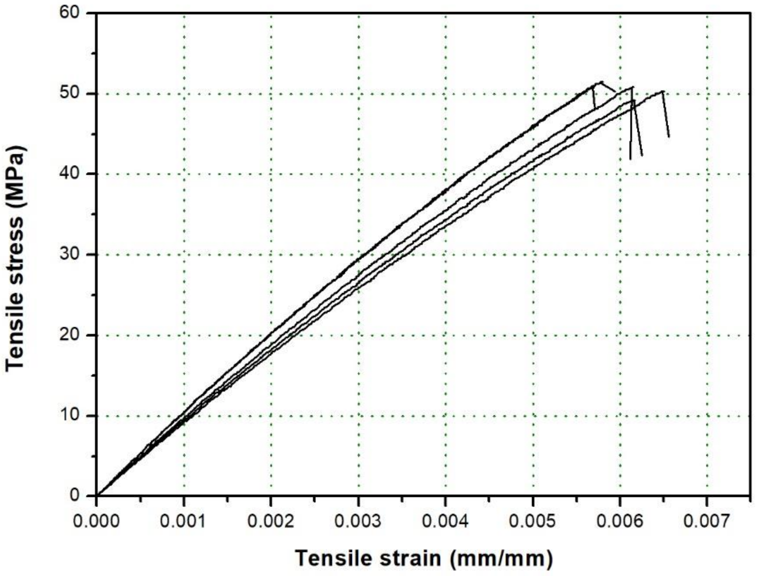

Figure A.25: Five replicate tensile stress -strain curves of DGEBA /2% CS after one month of exposure to accelerated weathering

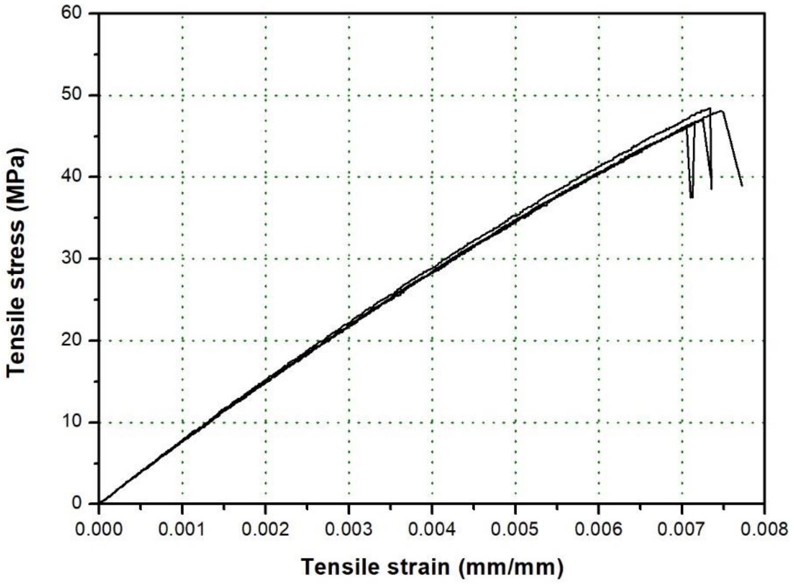

Figure A.26: Five replicate tensile stress -strain curves of DGEBA /2% CS after two months of exposure to accelerated weathering

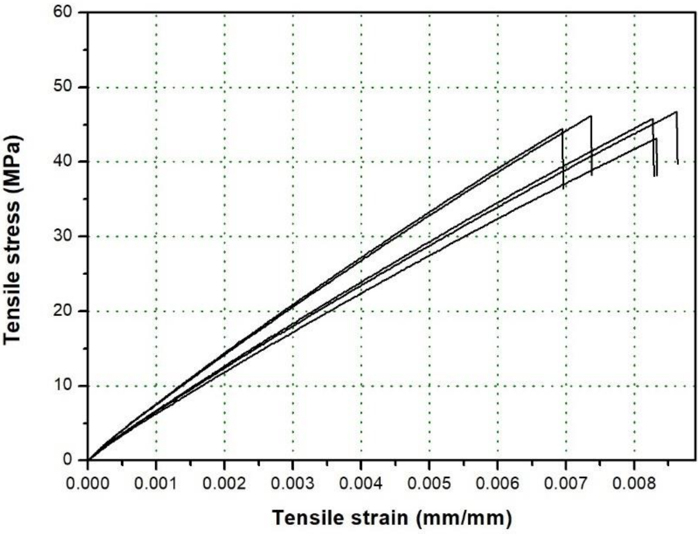

Figure A.27: Five replicate stress -strain curves of DGEBA /2% CS after three months of exposure to accelerated weathering

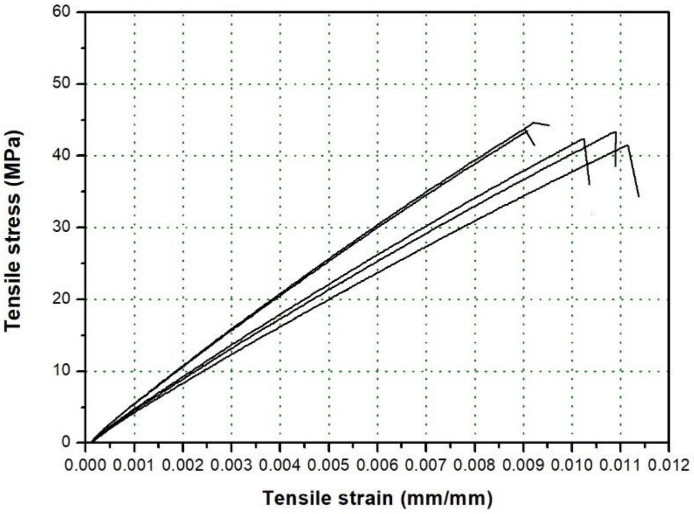

Figure A.28: Five replicate stress -strain curves of DGEBA /2% CS after four months of exposure to accelerated weathering

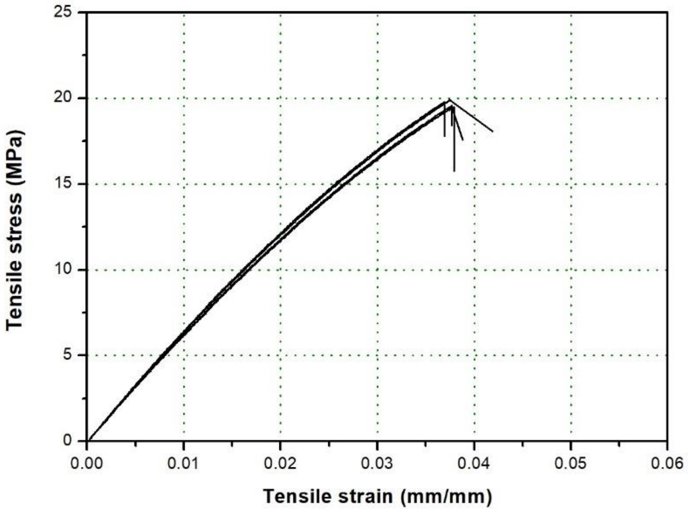

Figure A.29: Five replicate stress -strain curves of HDGEBA /2% CS after one month of exposure to accelerated weathering

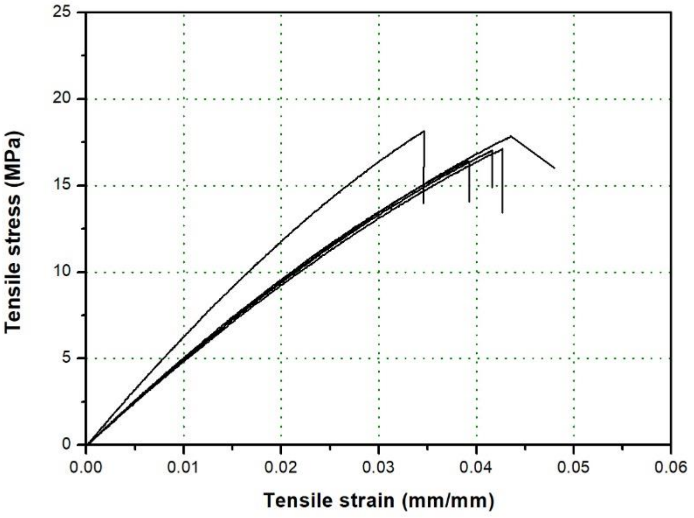

Figure A.30: Five replicate stress -strain curves of HDGEBA /2% CS after two months of exposure to accelerated weathering

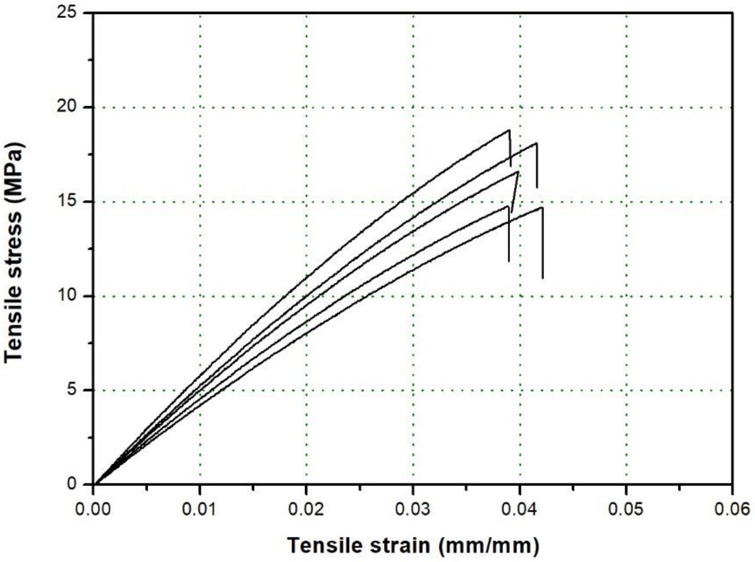

Figure A.31: Five replicate stress -strain curves of HDGEBA /2% CS after three months of exposure to accelerated weathering.

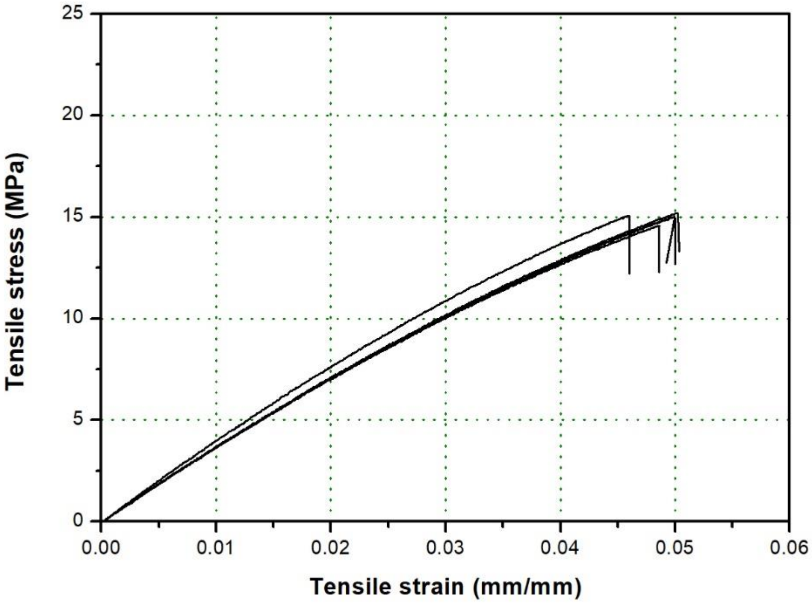

Figure A.32: Five replicate stress -strain curves of HDGEBA /2% CS after four months of exposure to accelerated weathering

Appendix Part B

Thermal Degradation (TGA)

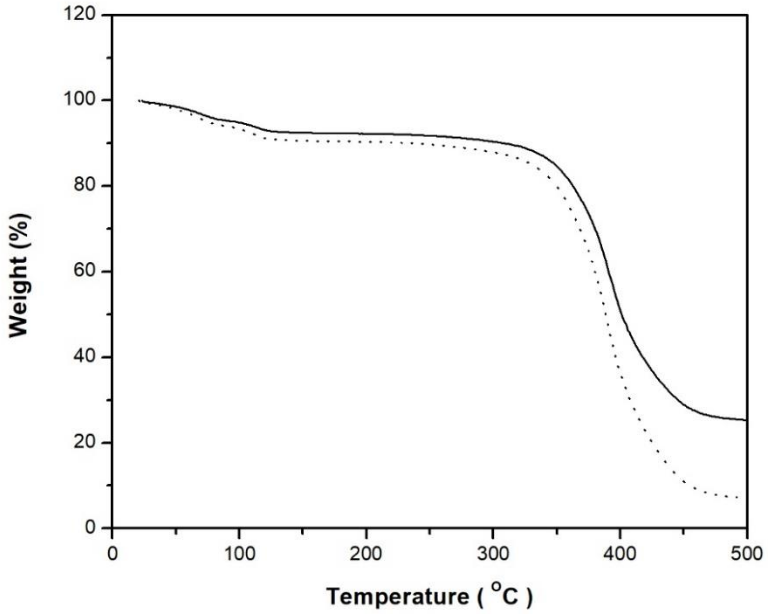

Figure B.1: TGA comparison of DGEBA epoxy before (solid line) and after (dotted line) exposure to six months accelerated weathering

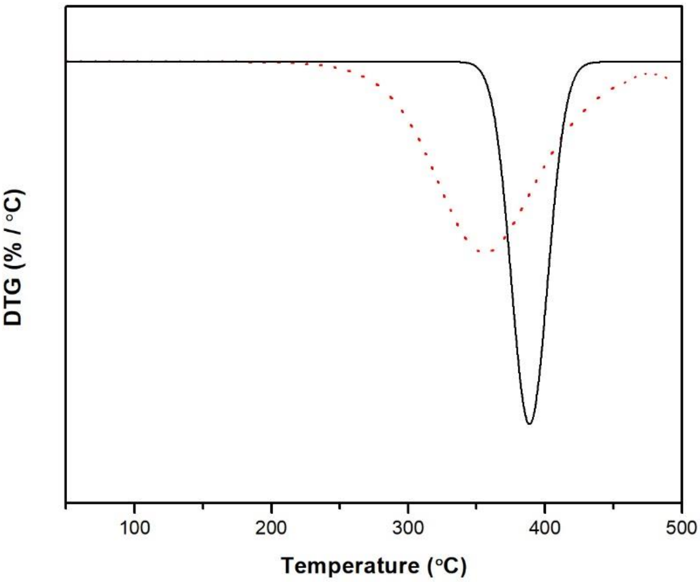

Figure B.2: DTG comparison of DGEBA epoxy before (solid line) and after (dotted line) exposure to six months accelerated weathering

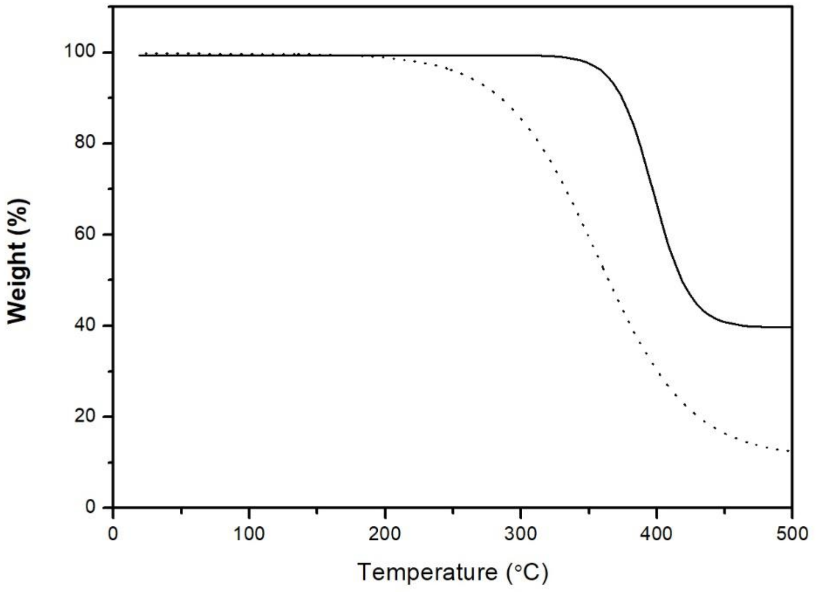

Figure B.3: TGA comparison of HDGEBA epoxy before (solid line) and after (dotted line) exposure to six months accelerated weathering

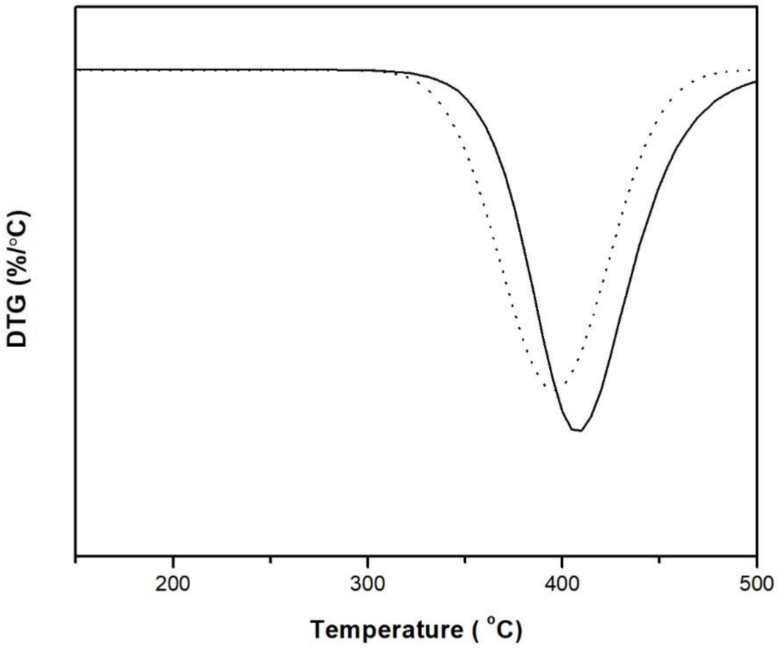

Figure B.4: DTG comparison of HDGEBA epoxy before (solid line) and after (dotted line) exposure to six months accelerated weathering

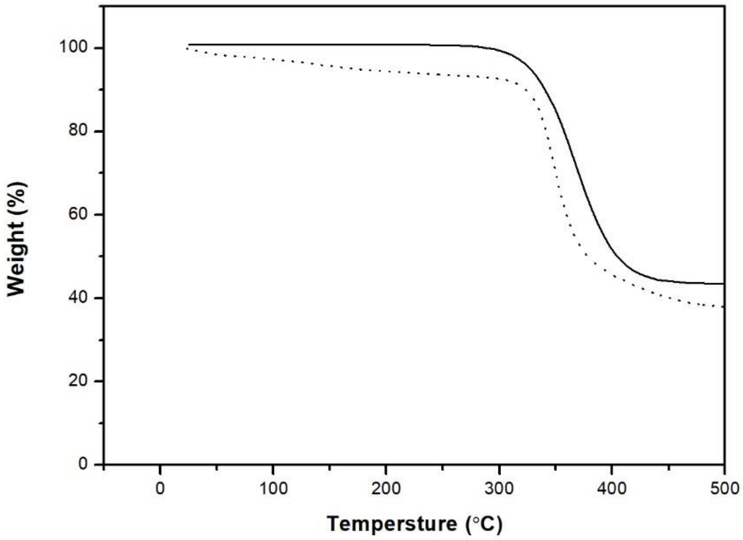

Figure B.5: TGA comparison of epoxy DGEBA /0.5% MWCNT before (solid line) and after (dotted line) exposure to six months accelerated weathering

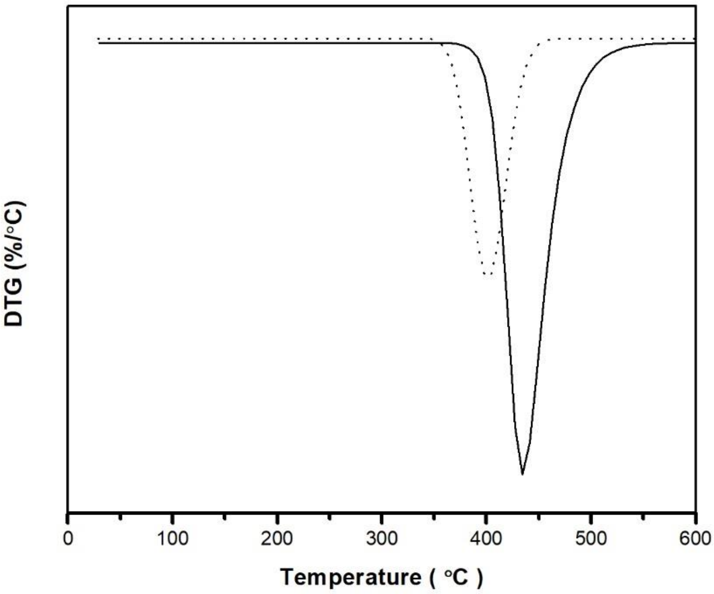

Figure B.6: DTG comparison curves of epoxy DGEBA/0.5% MWCNT before (solid line) and after (dotted line) exposure to six months accelerated weathering

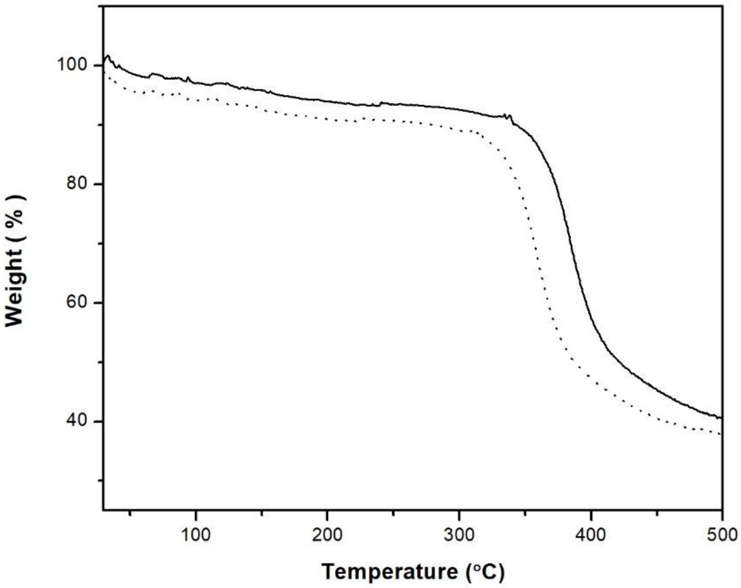

Figure B.7: TGA comparison of HDGEBA / 0.5% MWCNT composite before (solid) and after (dotted) exposure to six moths accelerated weathering

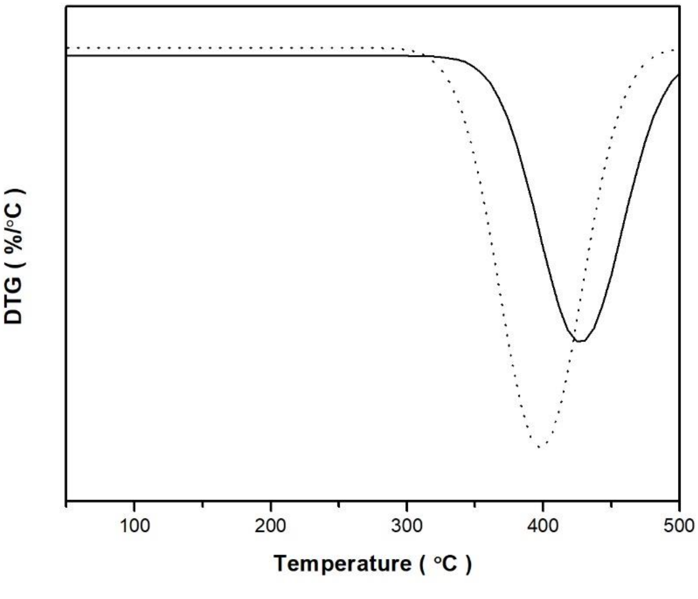

Figure B.8: DTG comparison thermogram curves of HDGEBA / 0.5% MWCNT before (solid line) and after (dotted line) exposure to six months accelerated weathering

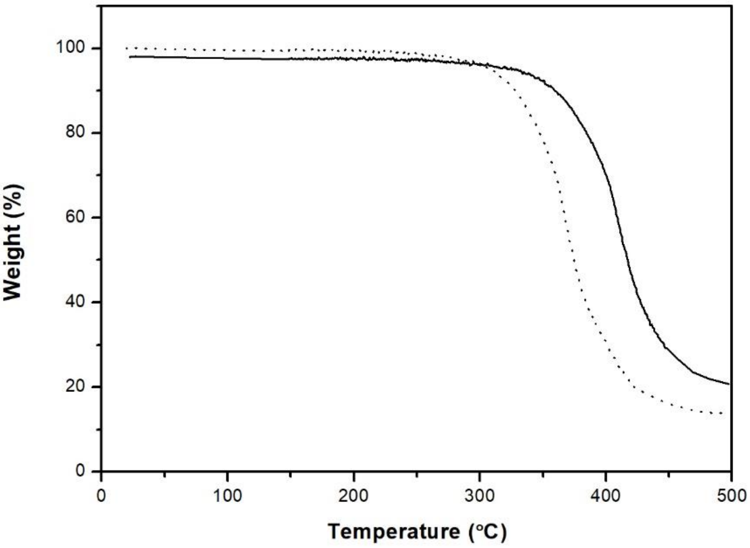

Figure B.9: TGA thermogram comparison curves of DGEBA / 2% MCC before (solid line) and after (dotted line) exposure to six months accelerated weathering times

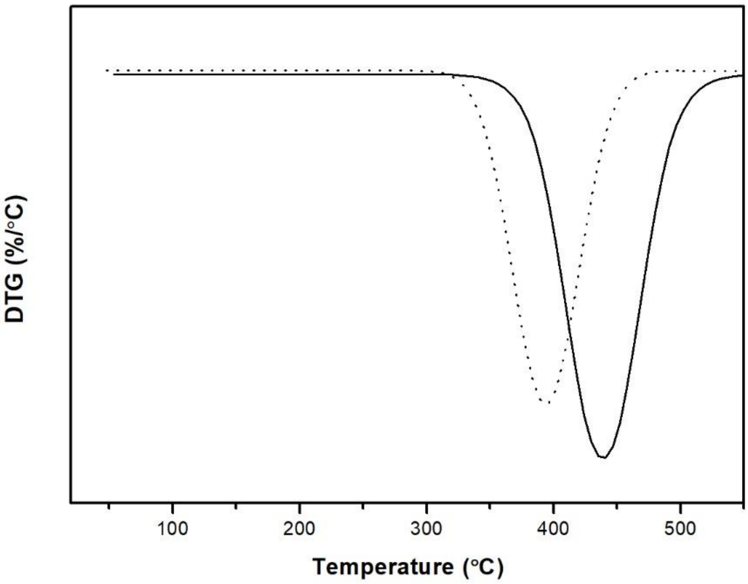

Figure B.10: DTG thermogram comparison curves of DGEBA / 2% MCC before (solid line) and after (dotted line) exposure to six months accelerated weathering

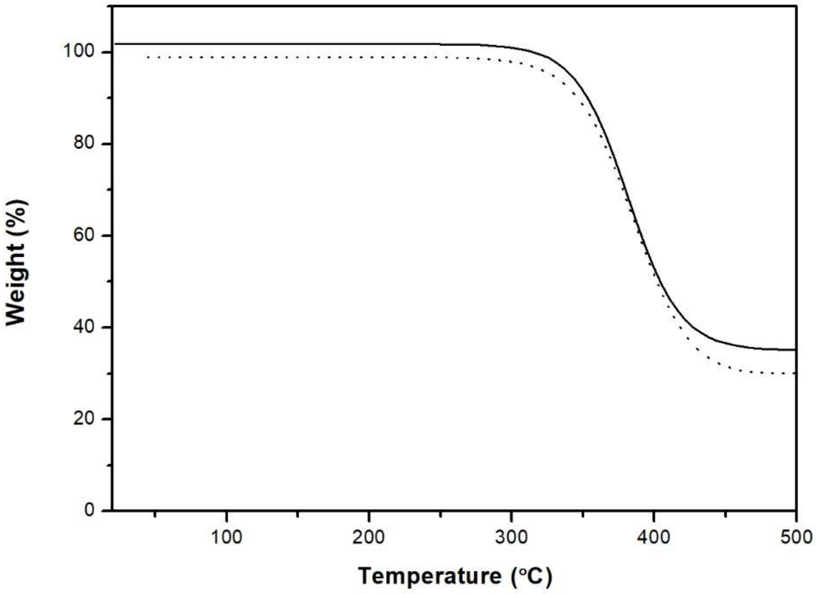

Figure B.11: TGA thermogram comparison curves of HDGEBA / 2% MCC before (solid line) and after (dotted line) exposure to six months accelerated weathering

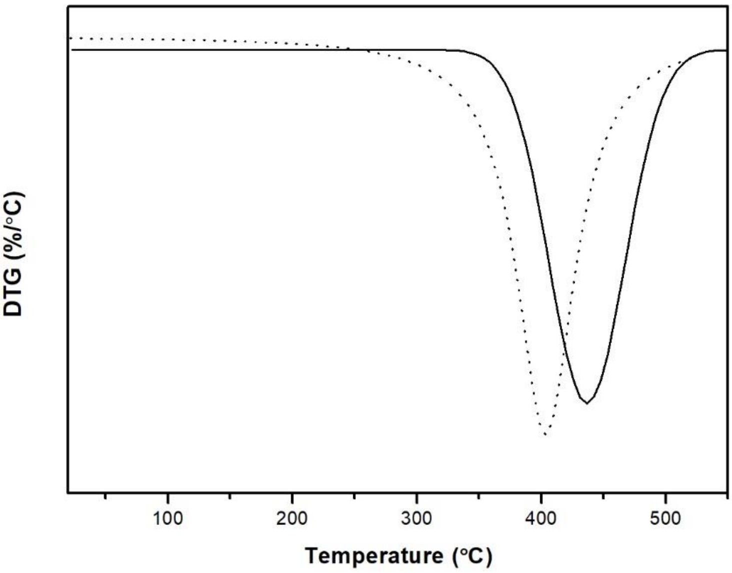

Figure B.12: DTG thermogram comparison curves of HDGEBA / 2% MCC before (solid line) and after (dotted line) exposure to six months accelerated weathering

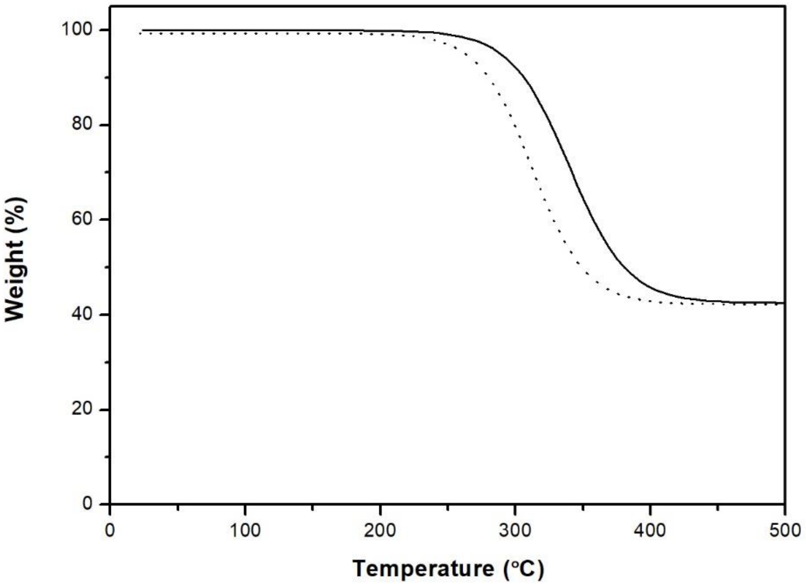

Figure B.13: TGA thermogram comparison curves of DGEBA / 2% CS before (solid line) and after (dotted line) exposure to six months accelerated weathering

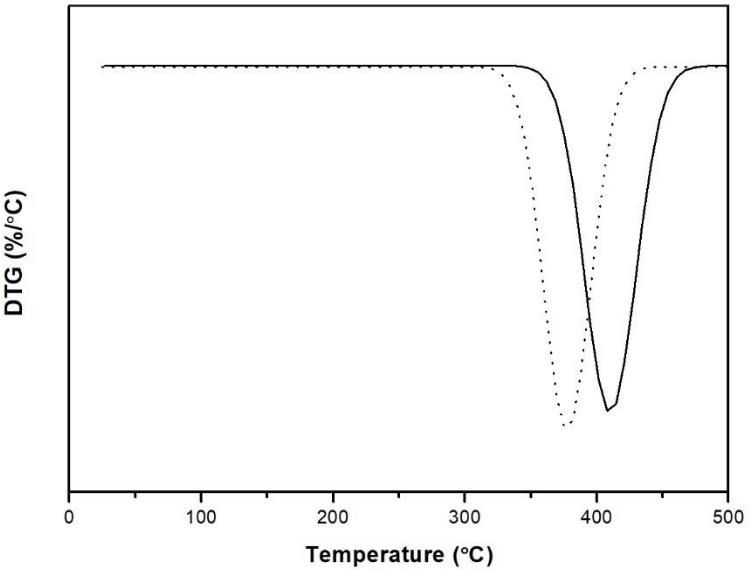

Figure B.14: DTG thermogram comparison curves of DGEBA / 2% CS before (solid line) and after (dotted line) exposure to six months accelerated weathering

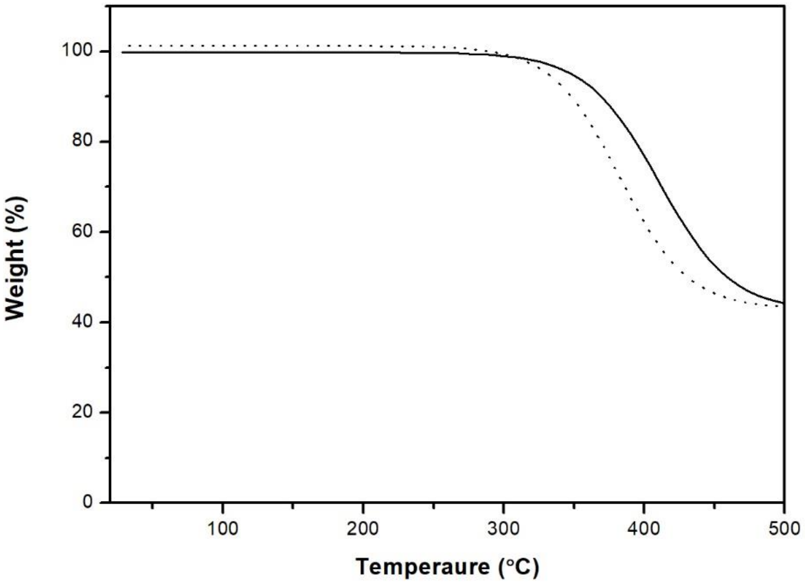

Figure B.15: TGA thermogram comparison curves of HDGEBA / 2% CS before (solid line) and after (dotted line) exposure to six months accelerated weathering

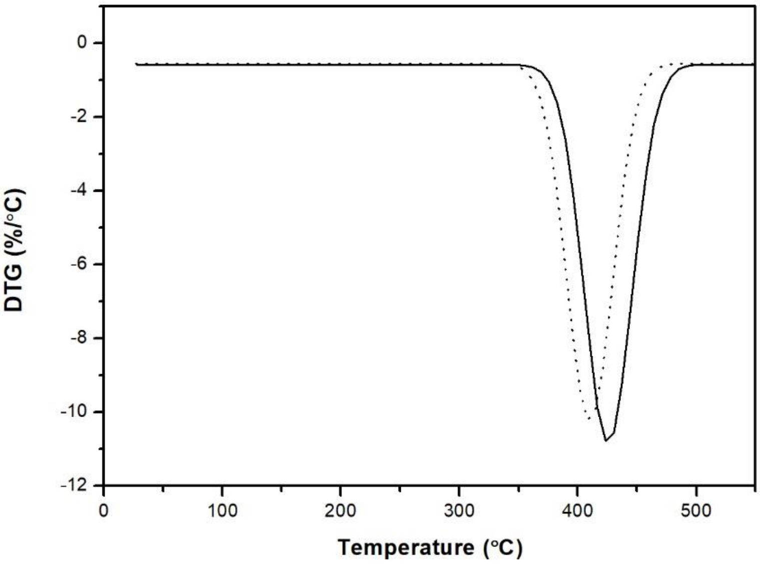

Figure B.16: DTG thermogram comparison curves of HDGEBA / 2% CS before (solid line) and after (dotted line) exposure to six months accelerated weathering