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THERMO-OXIDATION AND HYGROTHERMAL EFFECTS ON CYANATE ESTER POLYMER MATERIALS

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Zitao Liu

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THERMO-OXIDATION AND HYGROTHERMAL EFFECTS ON CYANATE ESTER POLYMER MATERIALS

By

Zitao Liu

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

THERMO-OXIDATION AND HYGROTHERMAL EFFECT ON CYANATE ESTER POLYMER MATERIALS

By

Zitao Liu

The aim of this research is to study thermo-oxidation and hygrothermal effects on cyanate based polymer materials. Cyanater ester (CE) and siloxane-modified cyanate ester (SMCE) and their graphite composites were investigated. Gravimetric experiment, differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), three-point bend tests were employed to study the mechanical and physical mechanisms of thermo-oxidation on cyanate based polymer materials. Water absorption experiments and three-point bend tests were used to characterize the water diffusion and hygrothermal degradation of cyanate based polymer materials.

Thermo-oxidation experiments showed that SMCE gains weight when aged in the air at 100°C but shows virtually no weight gain when aged in argon at 100°C. CE resins show no weight gain when aged in the air or argon at 100°C.

Differential scanning calorimetry (DSC) tests show that glass transition temperature of SMCE decreases about 35°C after aged in the air at 100°C for 3.4×10^6 sec (~ 40 days). Three-point bend tests indicated that the flexure strength of SMCE decreased by 20% after aging in the air for 7.63 $\times10^6$ sec (~ 3 months). FITR results provide information on the bonding character and chemical structure of CE & SMCE materials in this research. Results suggest SMCE degrades at 100°C in the air due to the thermo-oxidation process. The degree of thermo-oxidation of the polymer resin depends strongly on the supply of oxygen from the environment and the diffusion of oxygen in SMCE resin.

Hygrothermal tests show water diffusion in cyanate ester based polymer and its composites is non-Fickian type. FTIR spectroscopy shows that water molecules diffusing into the polymer structure interact chemically with the cyanate ester polymer network. The interaction causes some water molecules to be trapped in the polymer network, thus the water absorption curves deviate from Fickian behavior. Calculation of activation energy supports the contention that water diffusion occurs mainly through the polymer matrix in the composite materials.

Three-point bend tests show that the flexure strength of CE and SMCE decreases with increasing aging temperature. The flexure strength of CE based composites decreases significantly only at high temperature. Results also show the surface degradation of SMCE and CE based composite materials and delamination of SMCE based composite materials after aging in 95°C distilled water for more than 2000 hours.

TO MY PARENTS

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LIST OF ABBREVIATIONS AND SYMBOLS

BMI	Bismaleimide
C.F./PEEK	Carbon fiber/polyetheretherketone composites
C.F./PSF	Carbon fiber/polysulfone composites
CE	Cyanate ester
D _c	Diffusion coefficients of composites
DFT	Delamination fracture toughness
DMTA	Dynamic mechanical thermal analysis
D _r	Diffusion coefficients of resin
DSC	Differential scanning calorimetry
E	Potential energy
ESEM	Environmental scanning electron microscopy
FTIR	Fourier-transform infrared spectroscopy
Gr/Ep	Graphite/Epoxy composite
Μ	Moisture concentration
M ₀	Initial moisture content

M _m	Equilibrium moisture content
M _t	Moisture content at time t
PEEK	Poly-ether-ether-ketone
РММА	Poly(methyl methacrylate)
PPS	Polyphenylene sulfide
Q	Activation energy
SEM	Scanning electron microscopy
SMCE	Siloxane-modified cyanate ester
Tg	Glass transition temperature
UV	Ultraviolet
w%	Weight percentage change
wo	Original weight of samples
w _t	Weight of aged samples

Chapter 1

INTRODUCTION

Polymer composite materials [1-7], especially epoxy resin matrix composites, have been used for decades in the electronics, aerospace, sporting goods and automotive industries due to their high strength, excellent dielectric properties, high dimensional stability and low specific weight. One of the major concerns of composite materials [4-9] in industry and commercial applications has been their long-term durability under environmental conditions such as moisture, temperature, oxygen and radiation. These effects, particularly the effects of moisture absorption and oxidation on polymer and polymer composite materials, have been extensively studied since the early 1970s [4-12].

Most investigations [4-12] have shown that epoxy based composite materials absorb significant amount of water which often induces the degradation and dimension instability of polymer materials. Such changes tend to limit their application in hightechnology industries which usually demands high environmental stability standards of materials. Intensive research [13-14] has been performed in effort to provide new thermosetting resins with a reduced tendency of moisture absorption without penalizing the processibility. Low moisture absorbing materials were achieved by the development of cyanate ester resin based materials [15-17].

Cyanate ester resin matrix composites reinforced by glass or aramid fibers established their presence in the application for multi-layer electric circuit boards as early

as the late 1970s [15]. The use of cyanate ester resins was pursued for circuit board applications for the following reasons: (1) The glass transition temperature of cyanate ester exceeds those of epoxy resins and match molten solder temperature (220°C-270°C); (2) low dielectric loss properties; (3) excellent (epoxy like) processibility; (4) low moisture absorption; (5) excellent adhesion to metals.

The significant reduction in water absorption of cyanate ester (CE) allows for much improved dimensional stability than epoxy based polymer materials. Improved dimensional stability makes CE very promising for applications in aerospace industry. Recently, successful efforts in toughening the cyanate ester resin by thermoplastic modifier such as siloxane-modified cyanate ester (SMCE) has led to a serious consideration of cyanate ester resin matrix composites for use in primary structure applications [14-16].

There have been several studies of thermo-oxidation effect on the durability of thermoplastic-toughened cyanate ester resin (Fiberite 954-2) and its composites by Paravatareddy et al. [17,18]. The samples were aged for periods of up to 9 months at 150°C and in one of three different gas environments: nitrogen, low pressure air and atmospheric ambient air. Results have shown the glass transition temperature of cyanate ester was affected substantially by the aging time and the environments, and the bending strength of the materials decreases by 30-40% over 6-month period at 150°C. But the thermo-oxidation mechanism of cyanate ester materials is still not clear. There has been no report on the thermo-oxidation effect on siloxane-modified cyanate ester materials.

There have been many studies on the hygrothermal effect on the cyanate ester based polymers materials [19-21]. Results show that the water absorption decreases the

glass transition temperature and mechanical strength of cyanate based polymer materials. But the mechanism of water diffusion in cyanate based material is still not clear and some conflicting results have been observed. Cinquin et al. [19] studied water absorption of cyanate ester materials and found the humidity absorption of cyanate ester follows Langmuir's law. Blair et al. [20] studied the moisture absorption of cyanate ester resin laminate. Their results showed that the moisture absorption curves of these materials follow Fick's second law of diffusion. Lee et al. [21] studied the water absorption of graphite fiber-reinforced cyanate ester resin composites. Their results showed these materials absorbed a remarkably small amount of moisture when exposure to high humidity and the moisture absorption curves follow Fick's law in the early stage of water absorption. They also observed that the degree of moisture absorption underwent a sudden increase to a new equilibrium level and the water absorption became non-Fickian after prolonged exposure to high humidity.

This research plans to investigate the thermo-oxidation effects and hygrothermal effects on CE and SMCE and their composites using gravimetric, analytical, and spectrographic techniques. The weight change of CE and SMCE has been measured subsequent to exposure in air and water environments at different temperatures. FTIR was used to monitor the chemical structure change during aging (thermo-oxidation) process. Glass transition temperature (Tg) of these materials was measured to study the extent of degradation of cyanate ester networks. Three-point bend tests were used to study environmental effects on mechanical strength of these materials. Further research will assess environmental effects on the polymer and composite interface. When completed, the efforts will clarify the mechanism of thermo-oxidation on cyanate ester

based materials and hygrothermal environment on cyanate ester based polymer and composite materials.

Chapter II

LITERATURE REVIEW

2.1 Cyanate Ester Based Polymer Materials

Cyanate ester resin, also known as cyanate ester, cyanic esters, or trizine resins, features the polymerizable functional group $-O-C\equiv N$ on an aromatic backbone. Like epoxies, these thermosetting resins are derived from bisphenols or polyphenols, and are available as monomers. All commercial dicyanate monomers fit the model compound structure illustrated below.



When heated, cyanide functionality undergoes cyclomerization to form symmetrically substituted trizine structures. This ring-forming addition polymerization results in a thermoset network of oxygen-linked trizine rings and bisphenol esters. Cured cyanate resins are classified as polycyanurates. The cyclotrimerization curing process is illustrated in Fig. 2.1 [22]



Dicyanate monomer



Prepolymer resin

Fig. 2.1 Formation of cyanate ester network from dicyanate monomers

The cyanate ester network has many interesting properties [23], such as high glass transition temperature (250-300°C), high toughness, low moisture absorption, good thermal stability, low dielectric constants, and excellent adhesion to metals. This combination of properties is unique in 250°C T_g resins and commends its use in high performance, technological applications, i.e., aerospace and electronic industries.

Polysiloxanes [24] as shown below are molecules with long Si-O-Si chains, side hydrocarbon groups and end functional groups. The chemical structure is shown as following:



X: -CN **R**: H **n**: 10-1000

Owing to the long Si-O-Si chains, polysiloxanes have a number of unique properties including low temperature flexibility, hydrophobicity, and ultraviolet and radiation resistance. It has been reported [24] siloxane-modified cyanate ester has better properties, such as high toughness, low water absorption and oxygen plasma stability, than the cyanate ester resin.

2.2 Thermo-Oxidation of Polymer Materials

Although all polymers degrade at high temperatures in a non-oxygen environment, degradation of polymers is much faster in the presence of oxygen at elevated temperatures. This phenomenon is often referred to as thermo-oxidation of

polymer materials [25-28]. The initiation of thermo-oxidation of polymer materials at elevated temperature is mainly due to the free radicals generated by thermolysis of polymer molecules [25-27]. The free radicals generated react rapidly with oxygen supplied by the environment. Thermo-oxidation reaction of polymer materials usually causes the degradation of polymers, i.e., lower tensile strength, lower glass transition temperature and lower dimensional stability. For high-temperature engineering polymer materials, thermo-oxidation degradation of these materials has been major concern for their practical application in high temperature environments.

2.2.1 Thermo-Oxidation Mechanism

In polymers, the oxidation propagates through a free-radial chain mechanism. The difference of thermo-oxidation from other chain reactions is that, besides the usual steps, i.e., initiation, propagation and termination, two additional important steps must be considered: (1) conversion of the formed hydrocarbon radials to peroxy radicals and (2) degenerate chain branching. A scheme including the most important steps in polymer oxidation is shown as follows [28]:

(I) Initiation

 $PH \rightarrow P' + H'$ PH is a carbon-hydrogen bond, P' and H' are free radicals

(II) Radical conversion

 $P + O_2 \rightarrow PO_2$ PO₂ is peroxide radicals

(III) Chain propagation

 $PO_2 + PH \rightarrow POOH + P$ POOH is peroxide hydrogen bond

(IV) Degenerate chain branching

$POOH \rightarrow \alpha P$

 $POOH + POOH \rightarrow \beta P$ (IV.2)

α P and β P are degenerated radicals

(V) Termination

$\mathbf{P} + \mathbf{P}$	\rightarrow	inactive product	(V.1))
		1		

$$P' + PO_2 \rightarrow \text{inactive product}$$
 (V.2)

$$PO_2 + PO_2 \rightarrow \text{ inactive product}$$
 (V.3)

(I) Initiation

The free radicals may be initialized by several external stimuli, such as light(photo-oxidation) and heat (thermo-oxidation), and will react most readily with molecular oxygen. Initiation by direct reaction of molecular oxygen with the polymer material and in step I has been observed during thermo-oxidation of polymers [28-30]. This reaction is endothermic and very slow at low temperatures. The probability of this reaction occurring is higher when the polymer contains reactive hydrogen. Researchers report [29,30] that tertiary-hydrogen and secondary-hydrogen adjunct electron-rich groups are very active.

The degenerate chain branching reaction (IV) (the decomposition of the hydroperoxides into radicals) may take over the role of initiation in the later phase of oxidation reaction. The chain branching produces a radical or radicals from a non-radical intermediate in the process. When peroxides are present in the original polymers, e.g.,

those formed during processing or storage, reaction (IV.1) may dominate the initiation reaction.

Audouin et al. [32] studied the mechanistic schemes of radical oxidation of hydrocarbon polymers in which initiation is only due to unimolecular or bimolecular hydroperoxide decomposition. The results of their kinetic analysis have been compared with data relative to the thermo-oxidation of polypropylene in solid state (60-160°C). Their results show the unimolecular initiation scheme is in good agreement with experimental results. The main characteristics of the unimolecular initiation scheme are: (1) the quasi-independence of the kinetic behavior with initial conditions, and (2) the initiation period depends only on the rate constant of unimolecular hydroperoxide decomposition.

(II) Radical conversion

The conversion of hydrocarbon radicals to peroxy radicals is very important because the majority of oxygen is absorbed by the polymer in this step. As soon as a radical is generated in an initiation reaction, it reacts very easily with the oxygen. Ground state oxygen is unusual in that it exists in the triplet state, i.e., it is a diradical. The reaction of alkyl radical with oxygen is essentially a radical coupling reaction that is very rapid in nature. The rate of this reaction, however, depends on the concentration of the oxygen inside the polymer, i.e., on its pressure outside and its ease of diffusion. Thus, with low oxygen pressure and/or with high sample thickness, the oxidation may become diffusion controlled.

(III) Chain propagation

Chain propagation in polymer oxidation consists of the hydrogen abstraction reaction of the peroxide radicals. When the rate constant of this reaction increases, the radical generated in step I and II will react faster with polymer molecules, generate more free radicals, and increase the rate of oxidation. The reactivity of hydrogen toward free radicals increase in the following order: primary<secondary<tertiary, in accordance with the decrease in bond dissociation energies [33]. Because of the high reactivity of the tertiary hydrogens, intermolecular propagation could be a major reaction path in the oxidation of some polymers such as polypylene and polystylene.

(IV) Degenerate chain branching

The decomposition of hydroperoxides to radicals is the most important step in polymer oxidation because of the formation of oxidation products [33]. The thermal decomposition of hydroperoxides can proceed unimolecularly, bimolecularly, or with the participation of RH groups, breaking down the polymer chains, forming new chemical groups such as carbonyl and carboxyl, and generating volatile products such as alcohols, acids, aldehydes.

(V) Termination

Unimolecular or bimolecular termination of free radicals are most common type of termination in polymer oxidation. Unimolecular termination is the reaction of alkyl radicals with molecular oxygen. The unimolecular termination usually occurs when solid polymer is oxidized in oxygen rich environment. Bimolecular termination is the reaction of two alkyl radicals forming an inactive particle. This process is very important at the low oxygen pressures.

2.2.2 Chemical Change of Polymers in the Oxidation Process

Fourier-transform infrared spectroscopy (FTIR) has been used to assess the chemical changes that occurs during thermo-oxidation process of hydrocarbon polymers [34-35]. FTIR results show that aldehydes (1735 cm⁻¹) and ketones (1720 cm⁻¹) are the main species present during the early stages of degradation, although carboxylic acids (1710 cm⁻¹) are the species dominating the later stages. The presence of carboxylic acids in the later stages indicates the chain scission of polymer molecules during the thermo-oxidation process. The chain scission of polymer molecules during thermo-oxidation usually generates small molecules and decrease mechanical properties of the polymers.

The thermo-oxidation of hydrocarbon polymers was investigated by Celina et al. [34] using FTIR spectroscopy. Polymer degradation was studied by measuring the spectroscopic changes that occurred during thermo-oxidation of polymers under air at temperatures ranging from 150 to 250°C. Their results show the formation of carbonyl groups and related oxidative reactions, weight loss and volatilization, as well as formation of conjugation and specific polymer reactions.

2.2.3 Effect of Chemical and Physical Structure on Oxidation

The chemical composition and structure of the molecules determine the thermooxidation stability of polymers. The rate of diffusion of oxygen into the polymer affects the rate of thermo-oxidation reaction. The rate of oxygen diffusion is much larger in the amorphous regions than in crystalline domains [36] because the crystalline core is inaccessible to molecular oxygen. This implies that the rate of oxidation is greater in the amorphous regions than in the crystalline regions. The mobility of radicals is also much

larger in amorphous regions than the crystalline regions. The diffusion rate of oxygen is also affected by the morphological degradation and the existence of oxygen containing groups built into the polymer.

The chemical structure of a polymer strongly affects its ability to resist oxidative degradation [37]. The rate of thermo-oxidation degradation may increase with increased chain branching of polymer structures, because polymers with branch chains have more tertiary hydrogen atoms than pure linear materials and the tertiary hydrogen atoms are more vulnerable to radical attack than are primary or secondary hydrogen atoms. The presence of double bonds in a polymer backbone also affects the mechanism of oxidative degradation because the radicals can react easily with double bonds. Oxidation products may also affect the rate of oxidation of the parent polymers. Many of the first formed oxidation products are more easily oxidized than the parent polymer.

2.3 Hygrothermal Effect of Polymer and Polymer Composite Materials

Polymer and composite materials absorb some amount of water slowly from its surroundings and this process is controlled by the diffusion of water in the polymer materials and environmental temperatures. The absorbed water often causes hygrothermal effects such as the degradation, plasticization, swelling, and lowered T_g of the polymer materials.

2.3.1 Water Absorption Kinetics

Moisture absorption process in polymer and polymer composites can be described by Fick's law of diffusion which can be expressed as

$$\frac{\partial M}{\partial t} = D \frac{\partial^2 M}{\partial x^2}$$
(2.1)

where M represents the concentration of the diffusing medium and x is a dimensional coordinate. By applying the appropriate boundary conditions and integrating, an expression predicting moisture absorption with time can be expressed as

$$\frac{M_{t} - M_{0}}{M_{\infty} - M_{0}} = 1 - \frac{8}{\pi^{2}} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^{2}} \times \exp\left\{\frac{-D(2n+1)^{2} \pi^{2} t}{h^{2}}\right\}$$
(2.2)

Where M_t , M_0 , and M_∞ are the moisture content at time t, the initial moisture content, and the equilibrium moisture content, respectively, D is the coefficient of diffusion and h is the sample thickness. The coefficient of diffusion, D, is given by:

$$D = \pi \left(\frac{h}{4M_{\infty}}\right)^{2} \left(\frac{M_{2} - M_{1}}{\sqrt{t_{2}} - \sqrt{t_{1}}}\right)^{2}$$
(2.3)

Diffusion coefficient depends on the environmental temperatures. The dependence of diffusion constant on temperatures follows the following expression:

$$D(T) = D_0 \exp\left(-\frac{Q}{RT}\right)$$
(2.4)

where D_0 is the diffusion constant. Q is the activation energy. T is the temperature.

The diffusion constant also depends on the physical properties of specimens. Rao et al. [38] studied the moisture diffusion characteristics of unidirectional composite specimens. They found that the diffusion coefficient of the composites is affected by the cut-edge surface area and by lay-up sequences of composite materials, which was attributed to tortuosity caused by fiber orientations.

Water absorption of some polymer materials has been observed to deviate from the Fick's law after prolong exposure to water. Chateauminois et al.[39] investigated the hygrothermal degradation of glass fiber/epoxy unidirectional composites. They showed water absorption can be described by Fick's law after short immersion times when water sorption occurs mainly by diffusion through the epoxy network. They noticed water absorption curves slowly deviates positively from Fickian behavior after a long time aging. The deviation was attributed to the occurrence of debonding at the interphase region during hygrothermal aging. They concluded that the hygrothermal degradation of the interface occurs essentially in the non-Fickian absorption steps when the epoxy matrix is close to saturation.

The Langmuir model is often used to describe non-Fickian water absorption. The Langmuir model assumes the absorbed water molecules exist in two phases, one free, as in the Fickian model, and the other trapped due to the interactions between the molecules of water and matrix. Coefficients were introduced into this model to account for the possible interactions between the water and polymer molecules. Cai et al. [40] studied the effects of non-Fickian water diffusion in fiber-reinforced polymeric composites. The departure from classical diffusion was attributed to the time-dependent response of polymers.

Langmuir-type two-step or one step model could be used to fit the experimental data. The Langmuir-type two-step model [41] can be represented by equation 2.5 and 2.6.

$$D\frac{\partial^2 n}{\partial x^2} = \frac{\partial n}{\partial t} + \frac{\partial N}{\partial t}$$
(2.5)

$$\frac{\partial N}{\partial t} = \gamma n - \beta n \tag{2.6}$$

Here, n is the number density of mobile molecules; N is the number density of bound molecules; γ is probability per unit time that during which a bound molecule of water become mobile; β is probability per unit time that a mobile molecule of water become bound; D is the coefficient of diffusion.

2.3.2 Plasticization and Tg Variation

Moisture absorption in most polymer and fiber-reinforced polymer composites is associated with a decline in the glass transition temperature (T_g) attributed to plasticization of the matrix. A number of material factors could influence the magnitude of the T_g drop including water content, absorption temperature, exposure history, composite moisture diffusivity, resin matrix chemistry and initial matrix properties. The influence of each of these factors must be keenly investigated to provide insight into the details of moisture absorption. Such critical insight is required to design polymer and composite materials systems with improved resistance to hygrothermal degradation.

Previous researches [42-46] have shown that the T_g of epoxy resins and Gr/Ep composites decreases as the water content increases. Kelly et al. [42] derived an expression to calculate the T_g of a plasticized system based on the free volume concept of polymeric materials.

$$T_g = \frac{\alpha_p v_p T_{gp} + \alpha_d (1 - v_p) T_{gd}}{\alpha_p v_p + \alpha_d (1 - v_p)}$$
(2.8)

Here, α is the expansion coefficient, ν is the volume fraction, and subscript p and d are for polymer and diluent, respectively.

Zhou et al. [44] found T_g depends not only on water content, but also on its exposure time and history. The longer the exposure time and higher exposure temperature, the less the drop in glass transition temperature. Cinquin et al. [19] studied the water absorption of composite materials based on different resin families: bismaleimide(BMI), cyanate and epoxy. Their data shows the glass transition temperature of cyanate ester based composites decreases more than BMI and epoxybased composites. Ma et al. [45] investigated the hygrothermal behavior of carbon fiberreinforced ploy(ether-ether-ketone) (PEEK) composites. They found the hygrothermal effect on the glass transition temperature of PEEK composites is negligible.

The glass transition temperature is reversible in most case which the material showing a recovery to the original T_g upon drying. Rice et al. [46] and VanLandingham et al. [47] evaluated the hygrothermal effects on the polyimides composite. They observed the glass transition temperature T_g was lowered with moisture absorption but was recovered when the sample was re-dried. Chateauminois et al. [39] investigated the plasticization of a glass/epoxy unidirectional composite by dynamic mechanical thermal analysis (DMTA). They found the plasticization effect on the thermo-mechanical property of the composite was temperature independent and reversible after re-drying of the aged material. In some polymer materials, however, moisture can cause irreversible degradation of polymer structure with the T_g change becomes irreversible. Xiao et al. [48] studied the hygrothermal aging effects on epoxy resin by FTIR, gravimetric tests and DMTA. The results show that water immersion at 50, 70, and 90°C lead to the

introduction of carbonyl groups in the resin and chain scission of the cross-linked structure. These irreversible structural changes induce an irreversible decrease of the glass transition temperature of epoxy resin.

A glass transition temperature increase was observed in some cases when the moisture diffusing into the polymer caused crosslinks of polymer molecules. Morgan et al. [49] studied the hygrothermal effects on BMI-carbon fiber composites using Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). Their result revealed that these resins are not fully cured and can continue to react as a result of dehydration-induced ether crosslinks. This further crosslinking causes T_g increases and mechanical property decreases.

2.3.3 Effect of Moisture Absorption on Mechanical Properties

Mechanical properties of fiber reinforced composite materials depend on those of their components, the fibers and the matrix plus the quality of the fiber matrix interface. A mechanism that results in the degradation of the matrix, fibers or their interface will result in a loss of characteristics of any structure made from composite materials.

Hygrothermal aging often cause the plasticization of polymer matrix with depression of T_g and swelling of specimen. These effects usually decrease the tensile properties of polymer and polymer composites. Mohd et al. [50] studied hygrothermal aging of nylon 66 and its carbon fiber-reinforced composites. They found hygrothermal aging reduced the tensile property of both unreinforced and reinforced nylon 66. This behavior was explained by moisture-induced plasticization and interfacial degradation. Haque et al. [51] studied the effects of moisture on tensile properties of Kevlar 49/epoxy, graphite/epoxy, single fiber and Kevlar 49-graphite/epoxy hybrid composites. Their

results showed variations in tensile strength, elastic modulus and Poisson's ratio with changes in the hygrothermal conditions. Their results indicated that moisture degrades the tensile strength of hybrid and single fiber composites.

Uschitsky et al. [52] studied the hygrothermal effect on epoxy filled with silica and alumina nitride particles. They showed that moisture diffusion leads to a decrease in the compound's strength and to a substantial increase in the material's plasticity. Bouadi et al. [53] studied the effects of moisture on Young's modulus, Poisson's ratio and material damping of the epoxy matrix. Their results showed that the effects of moisture were negligible at room temperature. As temperature increased, the moisture induced significant changes in Young's modulus and Poisson's ratio.

Hygrothermal effects also led in a temperature dependent decrease in fatigue properties of composite materials. Ma et al. [54] studied the hygrothermal effects on the fatigue behavior of the carbon/PEEK laminated composites. Their results indicated that the fatigue lives of immersed specimens were shorter than those without hygrothermal aging. Vauthieret et al. [55] studied the effects of hygrothermal aging on the fatigue properties of a unidirectional glass/epoxy composite. They found the endurance properties of the composite declined after water aging. Komai et al. [56] investigated the effects of water absorption on fatigue strength of carbon-epoxy composites. They found the fatigue lives of composite specimens decreased in water. They also found water absorption lowered the yield strength of the epoxy resin, changing the shape of the stressstrain curves of composites.

2.3.4 Hygrothermal Degradation of Polymer and Composite Materials

Degradation of composite materials may be caused by environmental exposure to humidity at increased temperature. The absorbed water could change the state of residual stress of composite materials and causes microcracks and delamination of composites.

Microcracking is a very important form of damage in composites. Microcracks could form pathways for the accelerated ingress of moisture and chemicals into the materials. Long-time exposure to hygrothermal environments could cause microcracks of polymer composite materials. Shirrell et al. [57] studied the exposure of epoxy composites to several different hydrothermal environments and examined the hygrothemally induced microcarcks by scanning electron microscopy (SEM). They observed severe microcracks at 82°C; the severity and frequency of these microcracks increased with relative humidity. Obst et al. [58] studied the evolution of microcracks under static and fatigue loading and the effect of microcracks on the mechanical performance. They found the presence of microcracks reduces the measured bearing strength as well as the interlaminar shear strength of the composite. Their results also showed a significant increase in the apparent diffusion coefficient in microcracked specimens.

Delamination is a very important failure mechanism of composite because it reduces the stiffness, strength and fatigue life of composite materials. Long-time exposure to hygrothermal environments could cause the delamination of polymer composite materials. Several studies [6,7,59] show that moisture absorption of thermoset polymer composite degraded the delamination fracture toughness (DFT) of composite laminates. Lucas et al. [6] studied the water absorption on Model I (out-of-plane

loading) delamination of resin-matrix composites. Their results show significant reduction delamination fracture toughness occurred with moisture absorption under severe hygrothemal conditions. Other studies [59], however, reported the interlaminar fracture toughness of thermoplastic polymer composite increases as these materials absorb moisture. Hoa et al. [60] investigated the hygrothermal effect on Mode II interlaminar fracture toughness of a carbon/polyphenylene sulfide (PPS) unidirectional laminate. It was found that the interlaminar fracture toughness of the carbon/PPS laminate increases with both moisture content and temperature. Hooper et al. [61] studied the water absorption on Model I and Mode II delamination of graphite/epoxy composites. Their results revealed that moisture absorption tends to toughen the composite material. The difference in fracture toughness between thermoset and thermoplastic composite could be attribute to the fact that thermoset polymer composites absorbed much more moisture than thermoplastic polymer composite. The extra moisture in the thermoset composite degrades the matrix and matrix-fiber interface. losing the gain of fracture toughness from the plasticization of the matrix, that usually increases the fracture toughness.

Hydrolysis of some polymer network has been observed after a long time exposure to water. Mohd et al. [62] studied the injection molded short glass fiber reinforced poly(butylene terephthalate) subjected to hygrothermal aging. Examination of fracture surfaces using a scanning electron microscope (SEM) revealed the hydrolysis of the polymer matrix. They observed that the hydrolysis resulted in the formation of microvoids and degradation at the fiber-matrix interface.
2.3.5 Hygrothermal Effect on Interphase Phase

The fiber-matrix interface is a three-dimensional region around the fiber where properties are different from fiber and matrix. The performance of the composite is largely controlled by the strength of the bond across this interface. Water absorption has been shown to lead to a reduction in the mechanical properties of polymer composites [63-65]. This has been attributed, in part, to the hygrothermal degradation of fiber-matrix interface bond. Several researchers [63-66] observed that the hygrothermal conditions could cause an interfacial debonding in glass fiber/epoxy resin composites. Kaelble et al. [63] observed that the interlaminar shear strength could be reduced by 30-50% after immersion for 200 hours in 100°C water. They suggest that the degradation process is irreversible and is directly related to cumulative moisture degradation of fiber-matrix interfacial bond. Morii et al. [64] studied the weight changes in the interphase region of hygrothermally aged fiber-reinforced plastics. Their results showed that the weight gain in the interphase was caused by water penetration into the interphase region. They suggested that improvement in the water resistance of the binder at the interphase is important to enhance the water resistance of glass-fiber-reinforced plastics. Meyer et al. [65] investigated the long-term durability of the interfacial bond in carbon fiber polyetheretherketone (C.F./PEEK) and carbon fiber/polysulfone (C.F./PSF) composites after exposure to hygrothermal environments. Their results indicated that interfacial bond strength in C.F./PSF and C.F./PEEK composites is significantly influenced by longterm exposure to water, especially at high temperatures. Their results indicated that water saturation reduces interfacial bond strength in C.F./PSF and C.F./PEEK composites as a function of both time and temperatures. Sohn et al. [66] investigated hygrothermal

stability of graphite fiber/epoxy interphase. They found that the interfacial shear strength decreased gradually with water immersion time.

Chapter III

THERMO-OXIDATION OF CYANATE BASED POLYMER MATERIALS

3.1 Experimental

3.1.1 Materials

Fiberite 996HM and 954-3HM resins were used in this study. All the materials were received from Fiberite, Inc. Fiberite 996HM resin is a 177°C curing siloxanemodified cyanate resin with a -128°C to +121°C service temperature. Fiberite 954-3HM is 177°C curing cyanate resin with a - 128°C to +121°C service temperature.

The chemical structures of these materials are shown as follows Polysiloxane:



X: -CN R: H n: 10-1000

Cyanate ester monomer:



The nominal physical properties of 954-3 HM cyanate ester resin and 996HM siloxane-modified cyanate ester resin were listed in Table 3.1 and Table 3.2 [23]

Tensile Strength56.5 MPaTensile Modulus2.76 GPaFlexure Strength119.27 MPaFlexure Modulus2.96 GPaDensity1.19 g/cc

Table 3.1 Nominal physical properties of CE at room temperature

Table 3.2 Nominal physical properties of SMCE at room temperature

Tensile Strength	51.0 MPa
Tensile Modulus	2.96 MPa
Flexure Strength	75.8 MPa
Flexure Modulus	3.24 GPa
Density	1.146 g/cc

3.1.2 Specimen Preparation

All the samples were polished into 1 mm thick thin plate. Specimens of the dimension of 25 mm x 25 mm were cut form the plate using diamond saw. The weight of

the specimen ranged from 2 to 2.5 grams. The edges of the specimens were subsequently ground using 600 grit abrasive paper to achieve consistently smooth edge surfaces. All the samples were marked with a vibration pen and cleaned with methanol using ultrasonic cleaner. The samples were handled very carefully during the experiments to avoid any surface contamination.

3.1.3 Gravimetric Experiments

Samples were tested in an environmental test chamber consisting of gaseous aging environments of either ambient air or argon at 100°C. Gravimetric experiments were used to monitor weight of specimens during aging. Specimens were exposed to the aging environments for up to 3000 h. Specimens were taken out of the oven periodically during the aging experiment. Specimens were weighed using the analytical electronic balance with 0.01mg resolution. The experimental error of the measurement is $\pm 0.02\%$. The weight percentage change is calculated as follows

$$w\% = \frac{w_t - w_0}{w_0} \times 100\% \tag{3.1}$$

Where w% is the weight percentage change, w_t is the weight of aged samples, and w_0 is the original weight of samples.

3.1.4 Glass Transition Temperature Measurement

A TA Instruments 930 differential scanning calorimetry (DSC) system was used to determine T_g variations at different thermo-oxidation stages. Specimens of 3 mm x 3 mm x 1 mm were cut from the thermal aged samples at different time periods. The samples were sealed in small aluminum pans to prevent any weight loss during the experiment, and the weight of each sample pan was measured before and after each test. The samples were put into testing chamber protected by pure nitrogen gas. The temperatures range from 25° C to 350° C, and the temperature increase rate is 5° C/min. The T_g values were determined by the intersection of two tangential lines of the DSC curve before and after the glass transition regime.

3.1.5 Three-point Bend Test

Three-point bend flexure testing was performed to study the effects of thermooxidation on mechanical properties of both CE and SMCE. The standard procedure (ASTM D790-90) was used as guide for specimen preparation and testing. A representative sample of five specimens was tested for each aging condition, i.e., asreceived samples and samples aged for 1 and 3 months at 100°C in the air. Tests were conducted using Instron[®] mechanical test machine, with a 10 KN load cell. The nominal specimen dimensions used in this study were about 25 mm long, 3-5 mm wide and 1 mm thick. A cross-head speed of 2 mm/min was used in the test. For every experiment, 5 specimens were tested and the average data points were taken.

The flexure strength was calculated by formula

$$S = \frac{3PL}{2bd^2} \tag{3.2}$$

where $S =$	Flexure strength	(MPa)
P =	Breakload	(KN)
L =	Outer (support) span	(mm)
b =	Specimen width	(mm)
d =	Specimen thickness	(mm)

3.1.6 FTIR Testing

Infrared spectroscopy was used to determine the change of chemical structure of cyanate based polymer materials associated with bonding characteristics at various thermo-oxdation stages. A Nicolet 700 Series FTIR was used in this study. The cyanate polymer sample was polished to 0.025 mm thick thin film. The thin film was secured to a holder designed for FTIR test. The films with the holder were put into environmental chamber with dry air at 100°C for different periods of time up to 1200 h. The holder was taken out of the oven during different period of time. The sample was cool to room temperature in the air and transferred into the FTIR testing chamber.

3.2 Results and Discussion

3.2.1 Assessment of Thermo-oxidation of CE & SMCE by Gravimetric Experiments

To study the thermo-oxidation process of cyanate based polymer materials, cyanate ester and siloxane-modified cyanate were aged in an environmental test chamber consisting of either ambient air or argon at 100°C. Gravimetric experiments were used to monitored weight change of the specimens during thermal aging. The weight change of CE and SMCE are shown in Fig. 3.1. The graph shows that weight reduction of SMCE specimens was observed initially and followed with weight gain after 9h of exposure. The initial weight lose is due to the desorption of the moisture absorbed on the specimen surface.



Fig. 3.1 Weight change versus exposure time profiles are shown for siloxanemodified cyanate and cyanate ester resin materials aged in the air and argon at 100 °C.

The graph also shows the weight of the samples kept increasing with increase aging time up to 400 h. The surface color of SMCE specimens turns slowly from yellow to brown when aged in the air. Examination of specimen cross-section shows that the discoloration tended to start at the surface and gradually progress inward to the specimen interior. In contrast, no weight gain or color change was observed of SMCE when aged in the argon in excess of 6h. At the same time, only weight reduction was noticed in aging of CE both in the air and in the argon at 100°C. The weight lose is due to the evaporation of moisture absorbed on the sample surface.

To further confirm the thermo-oxidation process, experiments were conducted to study the weight gain of SMCE in different thermo-oxidation processes. In the first experiment (experiment A), samples were heated in the air at 100°C for 850 hours (step 1) and then heated in the argon for 400 hours (step 2). The results of experiment A are shown in Fig. 3.2. The graph shows SMCE specimens gain weight when they were aged in the air for 850 hours. The graph also shows SMCE didn't gain any weight when aged in the argon after they were aged in the air for 850 hours (step 1) then heated in the air for 1400 hours (step 2) and heated in the argon again (step 1) then heated in the air for 1400 hours (step 2) and heated in the argon again (step 3) for 400 hours. The results of experiment B are shown in Fig. 3.3. The graph also shows SMCE specimens didn't gain any weight when they were aged in the argon. The graph also shows that the samples start and keep gaining weight when they were aged in the air after aged in the argon for 200 hours. Both experiments show that the thermal degradation process ceased when the supply of oxygen in the aging environment was halted.







Fig. 3.3 Weight change of SMCE aged in the argon first and then aged in the air and aged in the argon again at 100°C (experiment B).

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Weight change %

Therefore, the role played by the supply of oxygen in the thermo-oxidation process of SMCE is key to understand the thermo-oxidation process. These results show SMCE gains weight only when oxygen is present in the environment. Therefore, the weight gain should be caused by the thermo-oxidation of SMCE by oxygen in the air. The results also show that pure CE didn't gain any weight when they were aged in the air or in the argon, which suggests that no thermo-oxidation occurred in the pure CE resin at this temperature. Siloxane-modified cyanate ester (SMCE) is cyanate ester (CE) modified with polysiloxane molecules, as shown in section 2.1. The distinguishing difference of their thermal aging behavior in the air suggests that the oxidation of SMCE could only be introduced by thermo-oxidation of the polysiloxanes, which was used to modify the cyanate ester resin.

For a more detailed assessment of thermo-oxidation process of SMCE in the air, we extracted data of the weight gain of SMCE aged in air from experiment A and experiment B and plotted them in Fig. 3.4. The graph shows that the weight gain curves in the thermo-oxidation of SMCE are nearly parallel. Both curves are linear with the square root of oxidation time.

Equation 3.3 to follow is the empirical relation of the average weight gain related to the aging time derived from the Fig. 3.4 is

$$w = w_0 + kt^{0.5}$$
, k=0.032 g·h^{-0.5} (3.3)

where w is the weight gain, w_0 is the original weight, k is a empirical constant (average slope of the curves).

Theoretically, thermo-oxidation of polymers usually involves two steps: (1) the diffusion of oxygen into the polymer and (2) the reaction of oxygen with polymer network groups. The rate of thermo-oxidation process is usually controlled by one of these two steps. For the diffusion controlled thermo-oxidation process, the weight change was found to be proportional to the square root of time, t^{0.5} [36]. It is distinguished from the chemical reaction controlled thermo-oxidation process, in which weight gain was found to be linearly related to time, t.

Equation 3.3 we derived from the experiments is found to be proportional to $t^{0.5}$, which suggests that thermo-oxidation of SMCE is controlled by the oxygen diffusion rate in the polymer network. Nam et al. [36] reported similar results. They observed the weight change of bismaleimide/carbon fiber composite during the thermo-oxidation process was controlled by oxygen diffusion, and the reaction rate was found proportional to t $^{0.5}$.

Thermo-oxidation of SMCE involves two basic mechanisms: (a) the diffusion of oxygen into the SMCE and (2) the chemical reaction associate with free radicals. Since the rate of thermo-oxidation reaction of SMCE polymer molecules with oxygen is much faster compared to the rate of diffusion of oxygen in siloxane-modified cyanate ester at $100 \,^{\circ}$ C below its glass transition temperature (169 $^{\circ}$ C), the process controlling thermo-oxidation in SMCE is the oxygen diffusion in the polymer network.



Fig. 3.4 Weight change of siloxane-modified cyanate ester aged in the air at 100° C

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Thermo-oxidation was not observed in the pure cyanate ester at 100 °C. Thermooxidation degradation of cyanate ester has been observed at temperature above 150 °C in the air [17,18]. This suggests that the initial temperature required for thermo-oxidation of cynanate ester is higher than for siloxane-modified cyanate ester. It was reported [24] that SMCE has lower degree of crystallinility than the cyanate ester. Researchers [29,30] have shown that the initiation temperature of thermal-oxidation increases with decreasing crystallinility of the polymers, which makes the structure more vulnerable to be attacked by oxygen.

Some authors [34,37,68] observed weight loss of the polymer sample during the thermo-oxidation of polyolefin polymer at temperatures above or close the glass transition temperature (usually above 200 °C). The weight loss was contributed to volatilization of small molecules generated by the oxidative reactions. In our experiments, the aging temperature (100°C) is much lower than the glass transition temperature (170°C) of siloxane-modified cyanate ester. At this temperature, the molecules generated by the thermal-oxidation reaction are more likely to stay in the polymer, increasing the weight of experiment samples

3.2.2 Degradation of Physical and Chemical Properties of CE & SMCE Materials

During thermo-oxidation process, polymer function groups react with oxygen molecules diffused into the polymer network. At the same time, the molecular chain scissions and rearrangement occurs, causing reduction of the molecular weight and changing the molecular weight distribution of polymers. The glass transition temperature (T_g) of the polymer also decreases because of chain fragmnetation and lower molecular species generated during the aging process.

Several authors[17,18,37]observed the decrease of the glass transition temperature during the thermo-oxidation of polymer. Hinsken et al. [37] studied the thermo-oxidation of polypropylene and found glass transition temperature decreases 25%. They also observed chain scission of the macromolecules. Gedde et al. [69] studied the thermo-oxidation of polyolefin in the hot air. They observed the decrease of T_g and degradation of the polymer by thermo-oxidation after a long time exposure to the hot air. The effect of thermo-oxidation on the durability of cyanate ester resin (Fiberite 954-2) has been studied by Paravatareddy et al. [17,18]. Their results show that the glass transition temperature of CE decrease substantially (10-30%) when aged in the air for 3 months at 150°C.

To evaluate the thermal degradation of SMCE and CE, we measured the glass transition temperature (by DSC) of both materials aged in the argon or air at 100°C and 140°C. The results are shown in Table 3.3 and Table 3.4. Table 3.3 shows that the glass transition temperature of SMCE decreases almost 20% (35 °C) when aged in the air at 100 °C for 40 days. On the contrary, Table 3.3 shows no change of T_g of SMCE when aged in the argon even at higher temperature (140°C). In comparison, cyanate ester resin samples show no decrease of T_g in both environments and temperatures, therefore, they show no sign of degradation.

Table 3.3 Glass transition temperature of CE aged in different environments (argon and air)

Materials (CE)	T _g (°C)
As received	240
Heated in Argon for 3.4x10 ⁵ sec (~ 4 days) at 140°C	240
Heated in the Air for 3.4×10^6 sec (~ 40 days) at 100°C	240

Table 3.4 Glass transition temperature of SMCE aged in different environments (argon and air)

Materials (SMCE)	T _g (°C)
As received	195
Heated in Argon for $.4x10^5$ sec (~ 4 days) at 140° C	195
Heated in the Air for 3.4×10^6 sec (~ 40 days) at 100°C	160

The decrease of glass transition temperature of SMCE suggests that the thermal degradation of SMCE takes place during the thermo-oxidation process. The difference in thermo-oxidation behavior of CE and SMCE is related to the chemical structure difference. The chemical structure difference of SMCE and CE (shown in section 2.1) suggests that the thermal degradation of SMCE is due to the thermo-oxidation of polysiloxane molecules, which may involve chain scissions of polysiloxane molecules.

To study the degradation of mechanical strength of cyanate ester based polymer materials during the thermo-oxidation, three-point bend tests were used to characterize effect of oxidation on the flexure strength of SMCE and CE before and after the thermal aging. The results were plotted in Fig. 3.5. Results from the three-point bend test of the CE and SMCE show a clear decrease of the flexure strength of SMCE. After being aged in the air at 100°C for 3 month, the flexure strength of SMCE decreased almost 20%. In comparison, the flexure strength of CE remains almost the same after aged in the air at 100°C for 3 months.

The decrease of the flexure strength of SMCE during the thermo-oxidation process may be due to the chain scissions of polysiloxane molecules. The chain scission breaks the long Si-O-Si bonds of polysiloxanes chains into smaller molecules. The flexure strength of the polymer will decrease when the polymer chains are degraded in the aging process.



Fig. 3.5 Three-point bend test of cyanate based polymer material (aged and as-received). Samples aged in the air at 100°C for 3 months

3.2.3 Thermo-oxidation Mechanism of SMCE

Infrared spectroscopy (FTIR) was used to determine the mechanism of thermooxidation and the change of chemical structure of SMCE. The sample was aged in the air at 100°C for more than 1200 hours. From the experimental results, shown in Fig. 3.6 a and 3.6 b, it was evident that the intensity of the peak at wavelength 1720-1730 cm⁻¹ increases with thermo-oxidation time. The decrease of the intensity of the peaks at 911 cm⁻¹ and 966 cm⁻¹ with increase aging time was also observed.

The peak at wavelength 1720-1730 cm⁻¹ is the characteristic absorption of carbonyl groups (-O=C-O-). The appearance and increase of this peak indicates a formation of carbonyl groups during the thermo-oxidation. The peak at wavelength 911 cm⁻¹ and 966 cm⁻¹ is the characteristic absorption of the CH bonds of the siloxane -SiOCH₂R group. The decrease of its intensity indicates a degradation of these groups in the thermo-oxidation process.

Several authors [34,35] observed similar functional groups formed in the thermooxidation process. Celina et al. [34] used FTIR spectroscopy to study polymer oxidation by measuring the spectroscopic change that occur during thermo-oxidation degradation of polymers exposed to air at temperatures ranging from 150°C to 250°C. Their results show that the formation of carbonyl groups during the thermo-oxidation reactions. Yoshitaka et al. [35] studied the thermo-oxidation degradation of poly(methyl methacrylate) (PMMA). They found that the initial period of the oxidation is characterized by a decrease in the intensity of absorption band of C-H groups.



Fig. 3.6 (a) FTIR spectra (1660 cm⁻¹ – 2380 cm⁻¹) of SMCE aged in the air. Change in the spectra with aging time shows the increase of the 1726 cm⁻¹ peak



Fig. 3.6 (b) FTIR spectra (765 cm⁻¹ – 1035 cm⁻¹) of SMCE aged in the air. Change in the spectra with aging time shows the decrease of 911 cm⁻¹ and 966 cm⁻¹ peaks.

From the experimental results we observed, a probable mechanism illustrating the experimental finding could be represented as following:

(1) Thermal initiation

Initiation by direct reaction of the polymer with molecular oxygen in step I has been observed during thermo-oxidation of most polymer materials [32-34]. This reaction is endothermic and very slow at low temperature. The probability of this reaction occurring is higher when the polymer contains reactive hydrogen or/and at elevated temperature. Researchers have reported [32-33] that tertiary hydrogen or secondary hydrogen close to electron rich group such as Si-O is very active. We observed the thermo-oxidation of SMCE happens at elevated temperature (100 °C). We also found that the absorption of C-H bonds of the siloxane -OSiCH₂R group decreases with aging time. These results suggest the initiation reaction of thermo-oxidation of SMCE is the breaking of C-H bonds of the siloxane -OSiCH₂R group as following:



(II) Radical conversion

This step usually involves the conversion of hydrocarbon radicals to peroxy radicals. This step is very important because the majority of oxygen molecules is absorbed by the polymer in this step. As soon as the **RHC**· is generated on side group in the initiation reaction, it reacts very easily with the oxygen, and the radical is quite stable below 300°C. During the thermo-oxidation of SMCE, we observed that the thermo-oxidation and degradation happens only in the oxygen surrounded environment at 100°C. The weight gain of SMCE can be explained by the reaction of these radicals with the oxygen diffused into the polymer. It also suggests the amount of oxygen absorbed is controlled by the rate of oxygen diffusion as observed in section 3.3.1. The whole scheme follows.



(III) Chain propagation

The radical generated in steps I and II kept react with siloxane molecules, generating more free radical on the side group $RHCO_2$. The rate of oxidation increases as the kinetic chain length becomes larger.

The radicals formed in this step also form more stable cyclic peroxide ring that has been observed in most thermo-oxidation of engineering polymers [29,30,70]. Researchers also observed that the cyclic peroxide ring in polysiloxane copolymer was formed by the intramolecular exchange reactions involving the Si-O bonds. During the thermo-oxidation of SMCE, a RHCO₂[•] radical can form a peroxide cyclic ring radical with a Si-O bond, which is chemically more stable than the RHCO₂[•]. The whole scheme follows.



(IV) Degenerate chain branching

The decomposition of hydroperoxides to radical is a very important step in polymer oxidation because the formation of oxidation products is caused by the degradation of these radicals. The thermal decomposition of hydroperoxides can break down the polymer chain, forming new chemical groups such as carbonyl and carboxyl, generating volatile products such as alcohols and acids.

As shown in section 3.2.2, the thermo-oxidation of SMCE accompanies decreases in the glass transition temperatures and flexure strength. It also suggested the degradation of SMCE by chain breaking of Si-O-Si chain of polysiloxane group during the thermo-oxidation process. FTIR results indicate the formation of carbonyl groups during the thermo-oxidation process. The gravimetric experiment only shows weight gain, which means no volatile products were generated in this process. These experimental results suggest that the decomposition of hydroperoxides during thermooxidation of this polymer involves breaking of Si-O-Si chain, forming carboxyl group with rearrangement of chemical structure and forming non-volatile products as following.



(V) Termination

Under most conditions [32-33], unimolecular or bimolecular termination of free radicals in polymer oxidation occurs almost exclusively. The reaction of alkyl radicals with molecular oxygen is very fast. The unimolecaur termination usually occurs when solid polymer is oxidized. This mechanism provides an explanation for rapid termination of thermo-oxidation of SMCE when the sample is removed from the oven and stored at room temperature.

3.3 Summary

The thermo-oxidation effect on cyanate based polymer materials can be summarized as follows:

• Gravimetric experiments show that SMCE gains weight when aged in the air at 100°C but shows no weight gain when aged in the argon at 100°C. Cyanate ester resins show no sign of weight gain when aged in the air or argon at 100°C.

• DSC tests show that glass transition temperature of aged SMCE decreases about

35°C after being aged in the air at 100°C for 40 days. Three-point tests show that the flexure strength of SMCE decreases about 20% after aged in the air for 3 months.

• FITR shows that thermo-oxidation process is going through the oxidation of the polysiloxane side group and breaking the main chain at the same time.

• Results suggest degradation of SMCE occurs at 100°C in the air through thermooxidation process. The process is controlled by the supply and diffusion of oxygen in SMCE.

Chapter IV

HYGROTHERMAL EFFECT ON CYANATE BASED POLYMER MATERIALS

4.1 Experimental

4.1.1 Materials

The materials under study were received from Fiberite Inc.: 996HM, 954-3 HM, M40J/996, UM55/954-3. Fiberite 996HM is a 177°C curing siloxane-modified cyanate resin with a -128°C to +121°C service temperature. Fiberite 954-3 HM is 177°C curing cyanate resin with -128 °C to +121 °C service temperature. M40J/996 is unidirectional carbon fiber (IM8) reinforced 996HM composite plate. UM55/954-3 is unidirectional carbon fiber reinforced 954-3 HM composite plate.

The chemical structures of these materials are shown as follows Polysiloxane:



X: -CN R: H n: 10-1000

Cyanate ester monomer:



The nominal physical properties of 954-3 HM cyanate resin and 996HM siloxanemodified cyanate resin have been listed in Table 3.1 and Table 3.2. The typical physical properties of cyanate resin composite and siloxane-modified cyanate resin composite were listed in Table 4.1 and Table 4.2 [23]

0° Tensile Strength	2 GPa
Modulus	290 GPa
90° Tensile Strength	27 MPa
Modulus	5.6 GPa
0° Compression Strength	407 MPa
Modulus	276 GPa

Table 4.2 Nominal physical properties of SMCE composite provided by manufacturer

0° Tensile Strength	2 GPa
Modulus	317 GPa
90° Tensile Strength	42 MPa
0° Compression Strength	890 MPa
Modulus	342 GPa

4.1.2 Hygrothermal Exposure

All hygrothermally-exposed samples were ground down to 1mm thickness. Specimens having the dimension of 25 mm x 25 mm were cut from the laminate with a diamond saw. The edges of the specimens were subsequently ground using 600 grit abrasive paper to maintain consistently smooth edge surfaces. The ratio of edge surface area to face surface area was 0.04 for all hygrothermally-aged specimens. Therefore, edge sorption effects were assumed to be negligible. The specimens were conditioned by heating at 100°C for 48 hours in the air to remove sorbed moisture on the surfaces and to eliminate residual stress caused by sample fabrications. Specimens were then placed in distilled water chambers at constant temperatures of 35° C, 65° C, 80° C and 95° C. The temperature variation is $\pm 2^{\circ}$ C. Specimens were weighed periodically. Once the specimens were taken out of the environmental chambers, the surface water was absorbed using a clean dry filter paper. Then, the samples were left for 2 min at the ambient

temperature and humidity conditions before weighing. Then specimens were weighed by using an analytical balance with 0.01 mg resolution. The experimental error of the test is $\pm 0.02\%$. The percentage moisture absorbed in the resin materials is calculated using equation 3.1

Optical microscopy, FTIR and environmental scanning electron microscopy (ESEM) were used to investigate surface modification associated with cracking and mass loss.

4.1.3 Three-point Bend Test

Three-point bend flexure tests were performed to study the effects of thermooxidation on mechanical properties of both CE and SMCE materials. In performing the flexure tests, ASTM D790-90 was used as a guide. A representative sample of six specimens was prepared and tested for each data point that relates to different aging temperatures. Tests were conducted using Instron[®] mechanical test machine with a 10 KN load cell. The nominal specimen dimensions used in this study were about 25 mm long, 3-5 mm wide and 1 mm thick. A cross-head speed of 2mm/min was used in this study. For every datum point, six specimens were tested and the average of these data points was plotted. The flexure strength was calculated by equation 3.2.

4.2 Water Absorption Results and Discussion

4.2.1 Water-absorption Kinetics of Cyanate Based Polymer Materials

Hygrothermal aging experiments of CE polymer and composite materials shows that the water-absorption curves follow Fick's law in the early stage, then the absorption curves deviate from the Fickian behavior, and become non-Fickian in the late stage of experiments.

Non-Fickian water-absorption of cyanate ester materials has been observed by some researchers [19,34]. They suggested that non-Fickian water-absorption is caused by chemical interaction or reaction of water molecules with cyanate ester polymer network. The chemical interaction traps extra water into the polymer network, causing samples keep gaining weight even after the saturation of water of polymer network. The chemically absorbed water was accounted for the non-Fickan behavior of cyanate ester polymers.

The chemical interaction also leads to hydrolysis of cyanate ester at high temperature. Researchers reported [21,71] that cyanate ester laminates stored in humid condition at high temperature encountered hydrolysis and blistering phenomena. They found that the cyanate ester blisters much easier than epoxies, although cyanate ester networks absorb less water than do epoxies. They suggested [67] that blistering is caused by the hydrolysis of the polymer network that produces gaseous products.

To study the water molecules interaction and reaction with the cyanate ester network, the FTIR spectrum of cyanate ester as-received and cyanate ester aged in the 95°C water for 3000h have been taken. The result is plotted in Fig. 4.1. The comparison of FTIR spectrum of hygrothermally-aged and as-received samples shows that some new absorption peaks appear (three peaks in the range of 3360-3340 cm⁻¹ and a peak at 1745 cm⁻¹) in the spectrum of cyanate ester aged in the water. The peak of the range 3360-3340 cm⁻¹ is related to N-H groups and the 1745 cm⁻¹ peak corresponds to C=O groups. These new chemical groups have been shown to be the product of water molecules reacting with -C=N groups of cyanate ester as shown in Fig. 4.2 [71].

The FTIR results suggest that the interaction which cause the non-Fickian water absorption of cyanate ester materials is chemical interaction of water molecules with the unlinked $-C \equiv N$ group of cyanate ester polymer network. The chemical interaction is most likely to be the hydrogen bonding of water molecules with the unlinked $-C \equiv N$ groups, given the fact that most organic compounds with unlinked $-C \equiv N$ groups tend to form hydrogen bonds with waters.





Fig. 4.1 FTIR spectra of cyanate ester resin aged in the water at 95° C for 3000hrs. The spectrum shows the increasing of 3360-3340 cm⁻¹ (N-H group) and 1745 cm⁻¹ (C=O group)



Fig. 4.2 The reaction of cyanate molecule with water forming N-H groups and C=O groups
4.2.2 Diffusivity in CE Based Polymer and Composites

In the Fig. 4.3-4.6, the weight change profiles are plotted for siloxane-modified cyanate, siloxane-modified cyanate carbon fiber composite, cyanate ester and cyanate ester based composite at the different temperatures. Symbols represent the experimental data of water absorption. Each data point was based on the average data of three samples. Because the ratio of thickness/width of the thin plate specimen was smaller than 4%, calculations of diffusion parameters were determined using a one-dimensional approach without incurring significant error.

As shown in Fig. 4.3, for siloxane-modified cyanate polymer, the water absorption curves at 35, 65,80 and 95°C was Fickian in the early stage of absorption, then became non-Fickian in the late stage of water absorption. The 95°C water absorption curve shows a slight weight reduction after being immersed in water for 1000 hours. As shown in Fig. 4.4, for siloxane-modified cyanate composite materials, the water absorption curves at 35, 65,80 and 95°C is Fickian in the early stage of absorption, then becomes non-Fickian. After being immersed in water for 1000 hours, a significant weight gain of samples aged at 95°C was observed.

As seen in Fig. 4.5, the water absorption curve of cyanate ester at 35, 65, 80 and 95°C is Fickian in the early stage of absorption, then becomes non-Fickian. At the late stage of the absorption curve, the curves of samples aged at 80°C and 95°C diverge from other samples. After being immersed in water for 1600 hours, the weight gain of samples immersed at 80°C and 95°C water is even more. At the same time, some blisters were observed inside the specimen.



Fig. 4.3 Water absorption curves of SMCE at different environmental temperatures with square root of time



Fig. 4.4 Water absorption curves of siloxane-modified cyanate fiber composite at different environmental temperatures with square root of time.



Fig. 4.5 Water absorption curves of cyanate ester at different environmental

temperatures with square root of time.



Fig. 4.6 Water absorption curves of cyanate ester fiber composite ester at different environmental temperatures with square root of time

As shown in Fig. 4.6, the water absorption curves of cyanate ester composite materials at 35, 65 and 80 °C are Fickian in the early stage of absorption, then become non-Fickian. The curve of specimen aged at 95°C diverges form this behavior in the late stage. A slight reduction in weight of the specimen has been observed after being immersed in water for 1000 hours.

The comparison of water absorption profiles of CE and SMCE (Figs. 4.3 and 4.5) shows that SMCE absorbed more moisture than the CE. This is contrary to the claim by the manufacturer (FiberiteTM)[23] that SMCE has lower moisture absorption than the CE. It is contended the greater of moisture absorbed by SMCE in our experiment is due to the thermo-oxidation degradation of SMCE when these specimens were conditioned in the air at 100°C before water absorption tests were conducted(shown in 4.2). Thermo-oxidation of the SMCE which involves chain scission of macromolecules and surface degradation made the material more susceptible to moisture absorption.

Assuming the temperature and moisture distribution in the material are uniform and following Fick's model in the early stage of diffusion, diffusivity of water in these materials can be calculated by equation 4.1

$$D = \pi \left(\frac{h}{4M_{\infty}}\right)^{2} \left(\frac{M_{2} - M_{1}}{\sqrt{t_{2}} - \sqrt{t_{1}}}\right)^{2}$$
(4.1)

All M. values used the saturation water absorption data before the water absorption curves deviates from the Fickian behavior.

The diffusivity calculated is list in Table 4.3-4.6.

Table 4.3 Diffusivity of CE resin

Temperature (°C)	35	65	80	95
D(mm ² s ⁻¹)	6.1x10 ⁻⁷	7.9 x10 ⁻⁷	9.2 x10 ⁻⁷	1.2 x10 ⁻⁶

Table 4.4 Diffusivity of CE composite

Temperature (°C)	35	65	80	95
D(mm ² s ⁻¹)	8.3 x10 ⁻⁸	1.6 x10 ⁻⁷	2.2 x10 ⁻⁷	2.5 x10 ⁻⁷

Table 4.5 Diffusivity of SMCE resin ester

Temperature (°C)	35	65	80	95
D(mm ² s ⁻¹)	2.88 x10 ⁻⁷	6.84 x10 ⁻⁷	1.32 x10 ⁻⁶	2.64 x10 ⁻⁶

Table 4.6 Diffusivity of SMCE composites

Temperature (°C)	35	65	80	95
D(mm ² s ⁻¹)	3.2 x10 ⁻⁸	7.5 x10 ⁻⁸	2.2 x10 ⁻⁷	5.1 x10 ⁻⁷

4.2.3 Activation Energy of Water Diffusion in Cyanate Based Polymer Materials

The Arrhenius plots of the logarithms of the diffusion coefficient versus 1/T for the neat resin and fiber composite are shown in Fig. 4.7 and Fig. 4.8. Solid circles represent the data of the neat resin and solid squares represent data of the composite.

The activation energy of diffusing was calculated by equation 4.2 by the slope of the Arrhenius plots.

$$\ln(D) = \ln(D_0) - \frac{Q}{RT}$$
(4.2)

where D_0 is the diffusion constant, Q is the activation energy.

Results show that the activation energy for the water diffusion in CE and CE composites is about 10 kJ and the activation energy for the water diffusion in SMCE and SMCE composites is about 24 kJ. The larger the activation energy, the more difficult for water to diffuse in polymer materials. Researchers reported [17-19] that polysiloxane molecules are hydrophobic. When the hydrophobic polysiloxane group is connected to the cyanate ester polymer network, the whole polymer network becomes more hydrophobic. Therefore, water diffusion is more difficult in the siloxane-modified cyanate ester than in a pure cyanate ester polymer network

The slopes of the Arrhenius plots of both SMCE resin and SMCE composite (Fig. 4.7) and CE resin and composite (Fig. 4.8) are almost same, indicating that water diffusion in both resin and composite occurs by the same diffusion process. The diffusion occurs through the bulk and/or the fiber-matrix interfacial region.



Fig. 4.7 The Arrhenius plots of the logarithms of the diffusion coefficient versus 1/T for cyanate ester and fiber composite.



Fig. 4.8 The Arrhenius plots of the logarithms of the diffusion coefficient versus 1/T of siloxane-modified cyanate ester and fiber composite

The transverse diffusion coefficient of the composite can be estimated from the diffusion coefficient of the resin, if all the fibers are parallel to the surface through which the moisture passes. Shen et al. [72] derived the expression:

$$D_c = D_r \left(1 - 2\sqrt{\frac{\nu_f}{\pi}} \right) \tag{4.3}$$

Where, D_c and D_r are the diffusion coefficients of composite and resin respectively. v_f is the volume fraction of carbon fibers.

The diffusion coefficients of both CE and SMCE composites were calculated from the diffusion coefficients of resins listed in Tables 4.3 and 4.5 using equation 4.3. The calculated data was plotted in the Figs. 4.7 and 4.8 to compare with the measured data of the diffusion coefficient of both CE and SMCE composites. The solid triangle in the Figs. 4.7 and 4.8 with dash lines represent the calculated data. Both Fig. s show that the agreements between measured and calculated values are quite close. The same agreement has been observed by several authors [15,73]. The agreement has been explained as the water diffusing only through the polymer matrix without any diffusing through the fiber-matrix interface in the composite. In some polymer and composite systems, researchers found large discrepancies [15,74]. The large discrepancies reported in the literature were explained by the degradation of fiber-matrix interface and the high diffusivity along poorly bonded fiber-matrix interfaces in the composite. The agreement of our data indicates that water diffusion in both CE and SMCE resin and composite occurs by the same diffusion process. The water diffusion in CE and SMCE composites is mainly through the matrix.

4.3 Hygrothermal Degradation of Cyanate Based Polymer Materials

The weight loss of SMCE at the 95°C shown in Fig. 4.3 can be attributed to the surface degradation of specimen. Fig. 4.9 is an ESEM photograph which compares the surface morphology of a sample aged in water for 3000h at 95°C with the surface of a non-aged sample. The micrography shows that some of the surface area of aged specimen was damaged by hot water. Some surface materials have been etched off the sample surface. The weight loss of cyanate ester composite materials at 95°C shown in Fig. 4.6 could be attributed to the observed surface degradation.

Fig. 4.10 shows the surface morphology of a CE composite specimen aged in water for 3000h at 95°C, compared with the surface of non-aged sample. The photograph shows that some surface area of the composite aged at 95°C was damaged. The damage occurs mainly at the resin rich region, and some micro-cracks were also observed on the damaged surface. Similar surface degradation [5] has been observed in hygrothermally aging of Graphite/Epoxy composite at 90°C.

The weight gain of SMCE composites at 95°C can be attributed to the delamination of composite laminate. Fig. 4.11 is an ESEM photograph of cross-section of a SMCE composite sample aged at 95°C compared with a non-aged sample. The cross-section photograph shows that the delamination happens inside the specimen. The delamination forms some large cracks inside of the specimen. These cracks could trap a large amount of water and cause a large increase of the sample weight as observed in Fig. 4.4.





(b)

Fig. 4.9 Surface morphology of aged siloxane-modified cyanate ester @95°C for 3000hrs (a) as-received, and (b) sample aged in water



(a)



(b) Fig. 4.10 Surface morphology of aged cyanate ester composite@95°C for 3000hrs (a) as-received, and (b) sample aged in water (The basket-weave imprint shown in both Figs. is due to the breather cloth used during processing of panels)



(a)



Fig. 4.11 Cross-section of aged siloxane-modified cyanate composite @95°C for 3000h (a) as-received, and (b) sample aged in water

4.4 Three-point Bend Test on Hygrothermally-Exposed Materials

To determine the hygrothermal effects on the strength of cyanate based polymer materials, three-point bend test was used to determine the flexure strength of these materials after exposed to water. Fig. 4.12 shows the results of three-point bend tests of hygrothermally-aged CE and SMCE. The graph shows a decrease of the flexure strength of SMCE with increasing aging temperatures. After aged in the air at 95°C for 3 months, the flexure strength of SMCE decreased almost 70%. The graph also shows a decrease in the flexure strength of CE with increasing aging temperatures. The flexure strength of cyanate ester decreased 20% after aged in the air at 100°C for 3 months.

During hygrothermal aging of SMCE and CE, especially in the high temperatures, hydrothermal degradation of cyanate ester and polysiloxane chains occurred. The flexure strength of these materials decreases when their chains break. The significant decrease of the flexure strength of SMCE at 80°C and 95°C could be attributed to the surface degradation of SMCE observed in Fig. 4.10 and thermo-oxidation of SMCE discussed in chapter 3.



Fig. 4.12 The results of three-point bend tests of the cyanate ester and siloxanemodified cyanate ester for 3000 hrs

Fig. 4.13 shows the results of the three-point bend test of the CE composites and SMCE composites after aged in the water at 100°C for 3 months. The graph shows no significant change of the flexure strength of the cyanate based composite materials when the aging temperature is lower than 95°C. The flexure strength of the CE composites and SMCE composites decrease significantly only at the high aging temperature (95°C). The flexure strength of SMCE composite decreased by almost 30% and the flexure strength of CE composite decreased by almost 20%.

The flexure strength of composite materials is mainly controlled by the strength of fibers and fiber-matrix interface [74]. As long as no environmental degradation of the fiber-matrix interface and fibers occurs, the flexure strength of composite materials should not affect significantly by the variance of environmental temperatures even there could be a degradation of polymer matrix. Fig. 4.13 shows no significant change of the flexure strength of the cyanate based composite materials when the aging temperature is lower than 95°C. When the temperature is above 95°C, thermal degradation of siloxane-modified ester and hydrolysis of cyanate ester polymer takes place. These effects could cause a significant decrease of the strength of the fiber-matrix interface of these composite materials. The degraded interface can cause the decrease of the flexure strength of SMCE and CE composites.



Fig. 4.13 The results of three-point bend test of the CE composites and SMCE

composites for 3000 hours

4.5 Summary/Conclusions

• Gravimetric measurement shows that the water diffusion curves of cyanate ester based polymer is non-Fickan type.

• Hygrothermal degradation of CE based polymer and composite materials have been observed at high temperature (95°C) after immersing in water for more than 2000 hours. Surface degradation of SMCE resin and CE composites was observed. Hydrolysis of cyanate ester polymer network with water molecules was also observed. Delamination of SMCE composites was also observed.

• The activation energy shows that water diffusion occurs mainly through the polymer matrix in the composite materials.

• The three-point bend test shows that the strength of CE based polymer materials decreases with increase aging temperature, and the strength of CE based composite materials is affected significantly by moisture at high temperatures.

Chapter V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The major results of this dissertation are concluded as following:

• The gravimetric experiment shows that siloxane-modified cyanate ester gain weight when aged in the air at 100°C. Cyanate ester resin gains no weight even after a long period of time.

• DSC testing shows that the glass transition temperature of aged siloxanemodified cyanate decreases about 20°C after aged in the air at 100°C for 40 days. The three-point bend tests show that the flexure strength of siloxane-modified cyanate decreases 20% after being aged in the air for 3 months. These results indicate that the polymer network degrades through thermo-oxidation process and that this process is controlled by oxygen diffusion in the polymer.

• FITR results show that the thermo-oxidation process starts with the oxidation of C-H bonds of the polysiloxane side groups. The reaction propagates with the breaking of the Si-O-Si chain and the formation of carbonic compounds.

• Gravimetric measurement shows that water diffusion in cyanate ester based polymer is non-Fickan type. The activation energy shows that water diffusion is only through the polymer matrix in the composite materials.

• Degradation of polymers and composites occurs at high temperature (95°C) after being immersed in water for more than 2000 hours. Three-point bend tests

show the strength of polymers decreases with increases in aging temperatures, and the strength of composites are affected significantly by moisture at high temperatures.

5.2 Recommendations

Many methods, such as FTIR, DSC, ESEM and three-point bend test, have been used to characterize the environmental effects on cyanate based materials. Also, more experiments are needed for a more complete understanding of environmental effects on cyanate based materials.

• Study thermo-oxidation effect on the mechanical behavior of cyanate

composite, especially the effect on matrix-fiber interface.

• Study thermo-oxidation of cyanate based polymer and composite materials in different temperature (from 80°C to 170°C).

• Hygrothermal effect on the delamination (Model I and Model II) of

composites.

BIBLIOGRAPHY

- D.Hull, <u>An Introduction to Composite Materials</u>, Cambridge University, London, U.K., 1981.
- Springer, G.S. (ED.), <u>Environmental Effects on Composite Materials</u>, v 1, Technical Publ. Co., Lancaster, PA, 1981.
- Springer, G.S. (ED.), <u>Environmental Effects on Composite Materials</u>, v 2, Technical Publ. Co., Lancaster, PA, 1984.
- 4. Springer, G.S. (ED.), *Environmental Effects on Composite Materials*, v 3, Technical Publ. Co., Lancaster, PA, 1988.
- 5. Zhou, J. and Lucas, J.P., Journal of Thermoplastic Composite Materials, v 9, n 4, Oct 1996, p. 316-328.
- 6. Lucas, J.P. and Zhou, J., JOM, December 1993, p. 37-40.
- 7. Lucas J.P. and Odegard, B.C., *Advances in Thermoplastics Composite*, STP1044, Newaz G., ed., 1989, p. 231.
- 8. Wang, C.S. and Chang, G.C., The effect of moisture absorption on composite laminates, *Composites Structures*, v 2, 1983, p. 260.
- 9. Joshi, O.K., The effect of moisture on the shear properties of carbon fiber composites, *Composites Structures*, v14, 1983, p. 196.
- 10. Wolff, E.G., SAMPE JOURNAL, v 29(3), 1984, p. 11.
- 11. DeNeve, D. and Shanahan, J.L., Polymer, v 34, 1993, p. 5099.
- 12. Adamson, M.J., Journal of Materials Science, v 15, 1980, p. 1736.
- 13. Grayson, M.A and Wolf, C.J., Proceedings of 5th International Conference on Composite Materials, San Diego, 1985, p. 1463.
- 14. Shimp, D.A., Christenson, J.R. and Ising, S.L, Proceedings of 34th International SAMPE Symposium, 1989, p. 222-233.
- 15. McConnell, V.P., Advance Composite, v 7(3), 1992, p. 28.
- 16. Speak, S.C., Sitt, H. and Fuse, R.H., Proceedings of 36th International SAMPE Symposium, 1991, p. 336.

- 17. Parvatareddy, H., Wang, J.Z. and Ward, T.C., Composites Science and Technology, v 53, 1995, p. 399.
- 18. Parvatareddy, H., Wilson, P.H. and Dillard, D.A., Composites Science and Technology, v 56, 1996, p. 1129.
- 19. Cinquin, J. and Abjean, P., Proceedings of 38th International SAMPE Symposium, 1993, p. 1539.
- 20. Blair, C. and Zakrzewski, J., Design of optical Instruments, SPIE 1690, 1992, p. 300.
- 21. Lee, F.W. and Lefebvre, P., Proceedings of 34th International SAMPE Symposium, 1990, p. 162.
- 22. David A S., <u>Cyanates, Guide to Engineering Plastics Families: Thermosetting Resins</u>, Elsevier Scientific Publishing Company, Amsterdam, 1992.
- 23. Fiberite data sheet of cyanate ester and cyanate siloxane resin from HEXCEL, October 15, 1995.
- Arnold, C., Mackenzie, P., Malhotra, V., Pearson, D., Chow, N., Hearn, M. and Robinson, G., Society for the Advancement of Material and Process Engineering (USA), 1992, p. 128-136.
- 25. Zolotova, N.Y. and Denisov, Y.T, Journal of Polymer Science, A1(9), 1971, p. 3311.
- 26. Iring, M. and Kelen, T., Polymer degradation and Stability, v 1, 1979, p. 287.
- 27. Holmstrom, A. and Sorvik, E.M., Journal of Applied Polymer Science, v 18, 1974, p. 761-779.
- 28. Kim, J.H. and Kwei, T.K., Chemical Engineering Communications, v 116, 1992, p. 105-116.
- 29. Schnabel, W. <u>Polymer Degradation: Principle and practical applications</u>, Elsevier Science Ltd Oxford Engl ,1981.
- 30. Kelen, T., *Polymer Degradation*, Elsevier Science Ltd Oxford Engl, 1982.
- 31. Gugumus, F., Polymer Degradation and Stability, v 52, n 2, 1996, p. 159-170.
- 32. Audouin, L., Gueguen, V., Tcharkhtchi, A. and Verdu, J., *Journal of Polymer* Science, Part A: Polymer Chemistry, v 33, n 6, p. 921-927.
- 33. Chien, J.C. and Boss, C.R., Journal of Polymer Science, A1(5), 1967, p. 3091.
- 34. Celina, M., Ottesen, D.K., Gillen, K.T. and Clough, R.L., Polymer Degradation and Stability, v 58, n 1-2,1997, p. 15-31.

- 35. Yoshitaka, T. and Seikichi, T., Journal of Applied Polymer Science, v 42, 1991, p. 2811-2817.
- 36. Nam, J.D. and Seferis, J.C., SAMPE Quarterly, v 24, n 1, Oct 1992, p. 10-18.
- 37. Hinsken, H., Moss, S., Pauquet, J.R. and Zweifel, H., Polymer Degradation and Stability, v 34, n 1-3,1991, p. 279-293.
- 38. Rao, R.M., Shylaja, H.V. and Suresh R., Journal of Reinforced Plastics and Composites, v 14, n 5, May 1995, p. 513-522.
- 39. Chateauminois, A., Vincent, L., Chabert, B. and Soulier, J.P., *Polymer*, v 35, n 22, 1994, p. 4766-4774.
- 40. Cai, L.W. and Weitsman, Y., Journal of Composite Materials, v 28, n 2,1994, p. 130-154.
- 41. Lee, M.C. and Nikolaos A.P., Journal of Applied Polymer Science, v 47,1993, p.1349-1359.
- 42. Kelly F.N. and Bueche, F., Journal of Polymer Science, L(1961), p. 549.
- 43. Mijovic, J. and Weinstein, S.A., Polymer Communication, v 26,1985, p. 237.
- 44. Zhou, J. and Lucas, J.P., Journal of Thermoplastic Composite Materials, v 9, n 4, Oct 1996, p. 316-328.
- 45. Ma, C.M., Huang, Y.H., Chang, M. and Sheu, M.F., Conference Proceedings In Search of Excellence 49th Annual Technical Conference -ANTEC '91, v 37, May 5-9, 1991, p. 2092-2096.
- 46. Rice, B.P. and Lee, C.W., Proceedings of the 1997 29th International SAMPE Technical Conference, v 29, 1997, p. 675-685.
- 47. VanLandingham, M.R., Eduljee, R.F. and Gillespie, J.W., Proceedings of the 1995 Symposium on High Temperature and Environmental Effects on Polymeric Composites, v 1302, Nov 13 1995, p. 50-63.
- 48. Xiao, G.Z. and Shanahan, M.E., Journal of Applied Polymer Science, v 69 n 2,1998, p. 363-369.
- Morgan, R.J., Shin, E.E., Lincoln, J.E., Choi, J. and Lee, A., Proceedings of the 28th International SAMPE Technical Conference, v 28, Nov 4-7 1996, p. 213-224.
- 50. Mohd Ishak, Z.A. and Berry, J.P., Journal of Applied Polymer Science, v 51, n 13, 1994, p. 2145-2155.
- 51. Haque, A., Mahmood, S., Walker, L. and Jeelani, S., Journal of Reinforced Plastics and Composites, v 10, n 2, Mar 1991, p. 132-145.

- Uschitsky, M. and Suhir, E., Proceedings of the 1997 ASME International Mechanical Engineering Congress and Exposition, v 21, Nov 16-21, 1997, p. 141-166.
- 53. Bouadi, H. and Sun, C.T., Journal of Materials Science, v 25, n 1B, 1990, p. 499-505.
- 54. Ma, C.M., Lee, C.L, Chang, M.J. and Tai, N.H., Polymer Composites, v 13, n 6, Dec 1992, p. 448-453.
- 55. Vauthier, E., Chateauminois, A. and Bailliez, T., Polymers and Polymer Composites, v 4, n 5, 1996, p. 343-351.
- 56. Komai, K., Minoshima, K. and Shiroshita, S., Proceedings of the Joint Japan-USA Seminar on Advanced Materials for Severe Service Applications, A143, n 1-2, 1990, p. 155-166.
- 57. Shirrell, C.D., <u>Advance Composite Materials. –Environmental Effects</u>, Vinson J.R. ed., ASTM STP 658, p. 21.
- 58. Obst, A.W., VanLandingham, M.R., Eduljee, R.F., Gillespie, J.W., Griesheim, G.E. and Tosi, K.F., Proceedings of 28th International SAMPE Technical Conference, v 28, Nov 4-7,1996, p. 34.
- 59. Wang, Q. and Springer, G.S., Journal of Composite Materials, v 23, 1989, p 434-447.
- 60. Hoa, S.V., Lin, S. and Chen, J.R., Journal of Reinforced Plastics and Composites, v 11, n 1, Jan 1992, p. 3-31.
- 61. Steven J.H and Ramaswamy, S., <u>Composite Materials: Fatigue and Fracture</u>, v 4, ASTM STP 1156, 1993, p. 318.
- 62. Mohd Ishak, Z.A. and Lim, N.C., *Polymer Engineering and Science*, v 34, n 22, Nov 1994, p. 1645-1655.
- 63. Kaelble, D.H, Dynes, P.J. and Crane, L.W., Journal of Adhesion, n5, 1975, p. 211.
- 64. Morii, T., Ikuta, N., Kiyosumi, K. and Hamada, H., Proceedings of the 1996 6th International Conference on Composite Interfaces, ICCI-6, May 5-8 1996, v 57, n 8, p. 985-990.
- 65. Meyer, M.R., Latour, R.A. and Shutte, H.D., Journal of Thermoplastic Composite Materials, v 7, n 3, July 1994, p. 180-190.
- 66. Sohn, D.W. and Sung, N., Proceedings of the ACS Division of Polymeric Materials: Science and Engineering, Apr 1990, v 62, 1990, p 43-47.
- 67. Iring, M., Szesztay, M., Stirling, A. and Tudoes, F., Journal of Macromolecular Science Pure and Applied Chemistry, A29, n 10, 1992, p. 865-884.

- 68. Song, J., Fischer, C.H. and Schnabel, W., *Polymer Degradation and Stability*, v 36, n 3, 1992, p. 261-266.
- 69. Gedde, U.W., Viebke, J., Leijstrom, H. and Ifwarson, M., Polymer Engineering and Science, v 34, n 24, Dec 1994, p. 1773-1787.
- 70. Abdel-bary, E.M. and Dessouki, A.M., Journal of Applied Polymer Science: Applied Polymer Symposium, v 55, 1994, p. 37-46.
- 71. Leo J.K., Idelette, H., Christopher W.M. and David A.S., Journal of Applied Polymer Science, v 64, 1997, p. 107.
- 72. Shen, C.H and Springer, G.S., Journal of Composite Materials, v 10, 1996, p. 1.
- 73. Zhang, Q. and Morgan, R.J., Journal of Composite Materials, v 27, 1993, p. 1465.
- 74. Thomason, J.L., Composites, v 26, 1995, p. 467.

