

Improving Adhesion between Carbon Fibers and Vinyl Ester Resins

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ABSTRACT

Free radical cured thermosetting vinyl ester resins have superior toughness and chemical resistance in comparison to unsaturated polyester. The use of vinyl ester composites reinforced with carbon fibers requires an improvement in the fiber-matrix adhesion levels. Previous data has shown that the application of a lightly cross-linked amine-cured epoxy sizing to the carbon fiber surface creates a beneficial interphase between the carbon fiber and vinyl ester resin matrix resulting in a substantial increase in fiber-matrix adhesion and the sizing has a optimum thickness^[1,2,8]. However, the exact mechanism by which this coating improved adhesion is not known. Vinyl ester resin can undergo as much as 10% volume shrinkage with cure while typical epoxy systems undergo only 3-4% shrinkage during cure^[4-6]. The cure volume shrinkage could have induced significant stresses in the fiber/matrix interphase. This could be the one of the most important factors that lowers the adhesion between carbon fiber and vinyl ester resin. In this study, the influence of the matrix cure volume shrinkage on the adhesion between carbon fiber and vinyl ester resin was investigated. Adhesion was evaluated as interfacial shear strength (IFSS) measured with a micro-indentation. Finite element analyses were used to simulate stress at the interphase and matrix as well after matrix shrink. It was found that cure volume shrinkage of vinyl ester could introduce thermal residual interfacial tensile stress which would decrease the adhesion between fiber and matrix, the greater the shrinkage the more significant the effect. The cure volume shrinkage was dependent on the molecular weight of the vinyl ester monomer and content of styrene content and also is related to the cure process and catalysts for polymerization. It was also found that a specially formulated epoxy-sizing which swells in a vinyl ester matrix could counteract the cure volume shrinkage of the matrix. The results from finite element analyses were consistent with the experimental results that larger shrinkage brought higher von Mises effective stress.

1. INTRODUCTION

Free radical cured thermosetting vinyl ester resins, typically contain 35~50% of styrene monomer as reactive diluents, have superior toughness and chemical resistance in comparison to unsaturated polyester. The use of vinyl ester composites reinforced with carbon fibers requires an improvement in the fiber-matrix adhesion levels. Previous data has shown that the application of a lightly cross-linked amine-cured epoxy sizing to the carbon fiber surface creates a beneficial interphase between the carbon fiber and vinyl ester resin matrix resulting in a substantial increase in fiber-matrix adhesion and the sizing has a optimum thickness^[2,3,7,8]. However, the exact mechanism by which this coating improved adhesion is not known. Upon cure, the volume shrinkage of vinyl ester resin is generally lower than that of unsaturated polyester resin but higher than that of their parent epoxy resin.

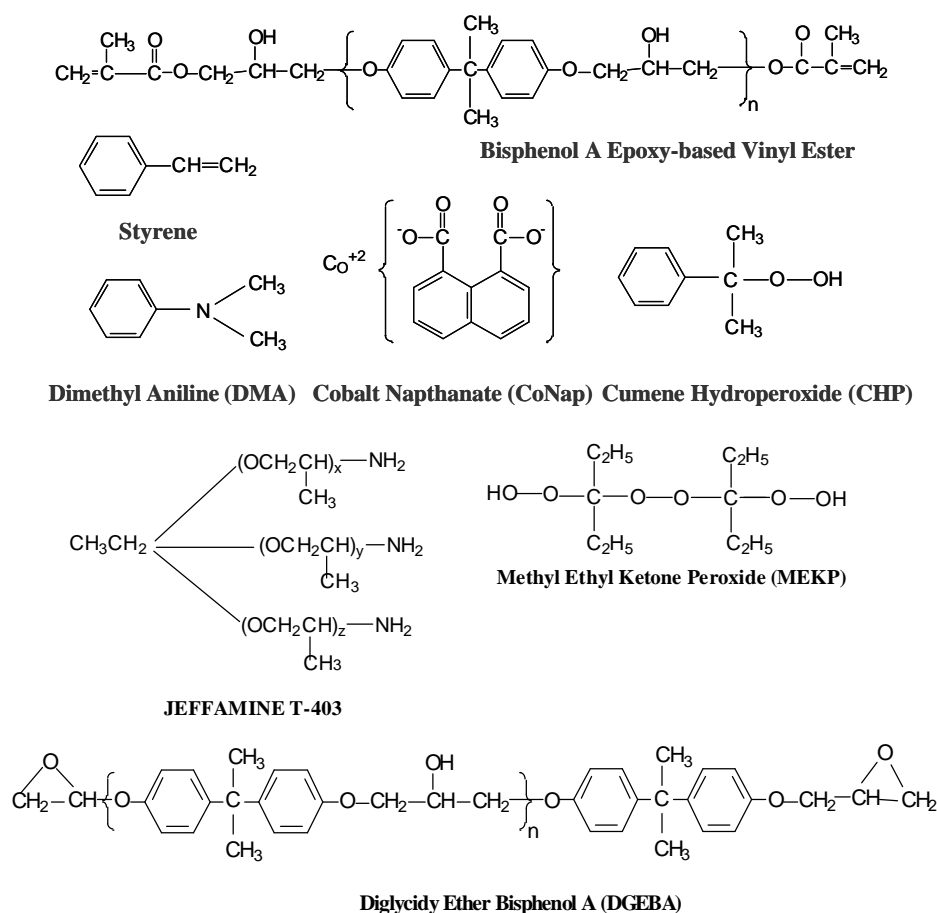
Vinyl ester resin can undergo as much as 5-10% volume shrinkage with cure depending on the molecular weight of vinyl ester monomer and the content of styrene, while typical epoxy systems undergo only 3-4% shrinkage during cure [4-6]. Most recently, a new-type epoxy vinyl ester resin which was claimed “free” of cure volume shrinkage [9] was made available. The objective of this study was to gain an understanding of the influence of matrix resin cure volume shrinkage on the adhesion between vinyl ester resin and carbon fiber.

2. EXPERIMENTS

Materials:

The fiber used in this study is an AS4 carbon fiber from Hexcel, Inc. The matrix resin is Derakane 411-C50 epoxy vinyl ester resin (D411-C50) from Dow Chemical and Fuchem 891 epoxy vinyl ester resin (Fuchem 891) from Shanghai Fuchem Chemicals Co. CHP-5 (diluted cumene hydroperoxide) from Witco Chemical and MEKP (methyl ethylketone peroxide) from Aldrich chemicals were used as the initiator. Both CoNap and DMA from Aldrich Chemicals are used as promoters and accelerators respectively. Diglycidyl ether of bisphenol A (DGEBA epoxy) and trimethylpropane amine (JEFFAMINE T403) are from Shell and Huntsman respectively. The molecular structures of the epoxy vinyl ester resins, the sizing epoxy material and the cure catalysts were shown in Fig. 1. Molecular weight of D411-C50 and Fuchem891 bisphenol A epoxy based vinyl ester are about 900g/mol and 1500~2000g/mol respectively. Both resin use styrene as reactive dilute. The styrene content of D411-C50 and Fuchem891 are 50% and 35% respectively.

Fig. 1 Vinyl Ester Resin, DGEBA Epoxy Sizing and the Catalysts



Methods

A lab-made dilatometer was used to measure cure volume shrinkage of vinyl ester resin from liquid resin to full cure. A digitally controlled, programmable oven was used for specimen curing to make sure all the samples were processed in the same way. The cure processes were same for all samples: room temperature for 1 hour, 90°C for 1 hour and 125°C for 1.5 hours. The cure recipes were recommended by the manufacturer or calculated from the recommended recipes based on the concentration of C=C bonds. The mixture of DGEBA and JEFAMINE T-403 was prepared and held for one half hour then added to acetone to form a 5wt% sizing solution. Fiber sizing was carried out by using a pre-impregnation machine. Thermal Gravimetric Analysis (TGA) was used to measure the thickness of the sizing. Dynamic Mechanical Thermal Analysis (DMTA), DMA 2980 from TA Instruments, and physical testing, was conducted to measure the mechanical properties of the matrix resin. A MTS nano-indentation instrument was used to measure the bulk moduli of the vinyl ester resins and quantify the gradient of the modulus between the sizing and the DGEBA epoxy and D411-C50 vinyl ester resin matrices. Nano-scratch was also carried out by the MTS nano-indentation machine. A RMC MT-7 ultramicrotome was used for preparing the nano-scratch sample surface with a diamond knife. Adhesion was evaluated as interfacial shear strength (IFSS) measured with a micro-indentation approach with the Interfacial Testing System (ITS). Finite element analyses were used to simulate the stress distribution around the fiber-sizing-matrix interphases during volume shrinking of the matrix resin and the micro-indentation process as well.

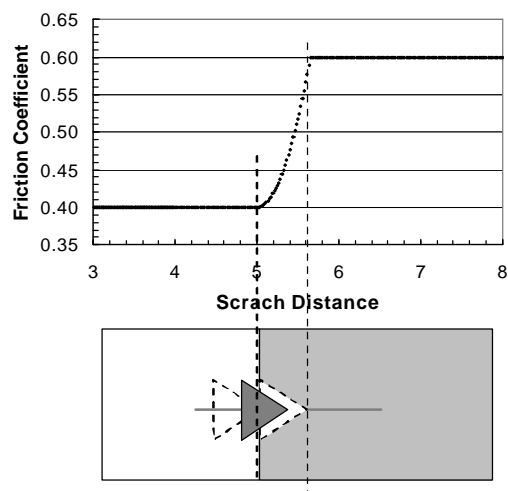
Effect of Indentation Tip Size of the Nano-Indentation Scratch Test

As shown in Fig. 2, the indenter size could enlarge a infinitesimal wide interface into a certain wideness region presenting in the out come scratch data. The indenter size depends on the depth of the scratch. The depth is determined by the hardness of the test material and the vertical load on the scratch tip. This scratch tip size and depth influence was simulated with a C++ program. The calculation was based on some reasonable assumptions.

Finite Element Analysis

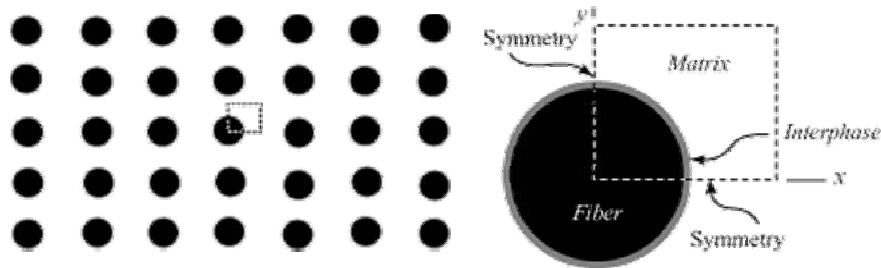
Consider the composite as an orthotropic material with regularly spaced fibers as shown in Fig. 3. A single fiber is singled out for simulation, and furthermore, only a quarter of this fiber is modeled because of symmetry. The dashed line indicated the representative volume element (RVE) that is simulated and is considered the fiber the nano-indenter would contact. This RVE is extended downward a length of 20 times the fiber diameter. The two sides of this dashed line intersecting at the fiber center represent symmetry planes for this repeating cell Fig. 3. Also shown in this figure is an interphase region between the fiber and matrix shown as a grey ring around the fiber. A commercial finite element code, LS-DYNA^[10], was used to model the matrix/interphase shrinkage and indenter contact. The explicit aspect of the code was used to model the matrix/interphase shrinkage followed by contact with the indenter. A thermal excursion was used to model the matrix/interphase shrinkage. A linear elastic, orthotropic, temperature dependent material was used. This material model is time-independent. Standard orthotropic elastic constants are E_a , E_b , E_c , ν_{ba} , ν_{cb} , ν_{ca} , ν_{bc} , G_{ab} , G_{bc} , and

Fig. 2 The effect of the tip size



G_{ca} . The thermoelastic constitutive behavior is defined by three, orthotropic coefficients of thermal expansion, \mathbf{a}_a , \mathbf{a}_b , \mathbf{a}_c , that produce normal strain components defined by $\mathbf{e}_i = \mathbf{a}_i \Delta T$, where T is the temperature. Note the coefficient of thermal expansion in the fiber directions are set to zero. This was done so the surface the top impacted remained plane. When these coefficients were not zero the matrix and interphase contracted considerably relative to the fiber making a domed surface for indenting. For the interphase two values are listed that represent the CTE for the 7.18% and 1.73% shrinkage. The higher CTE value is for the lower volume shrinkage because the temperature excursion was less in this case.

Fig. 3 A transversely isotropic array of composite fibers with the representative volume element indicated by a dashed line.



The simulation of the nano-indenter has two distinct phases: volume shrinkage of the matrix and interphase followed by loading by the indenter. Calibration of the volume shrinkage was done by iterating on different temperature changes to achieve the proper dilatation strain for the interphase and matrix. In all simulations the temperature change was decreased linearly. The temperature was held constant at the lowered temperature during the indenting phase of the simulation.

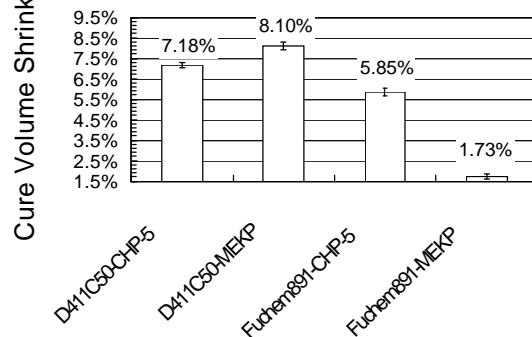
3. RESULTS AND DISCUSSION

Cure Volume Shrinkage of Vinyl Ester

Table 1 Cure Recipes

	Catalysts	Fuchem 891	D411-C50
CHP	CHP-5	1.40%	2.00%
	CoNap	0.21%	0.30%
	DMA	0.07%	0.10%
MEK P	MEKP	2.00%	2.85%
	CoNap	0.10%	0.14%

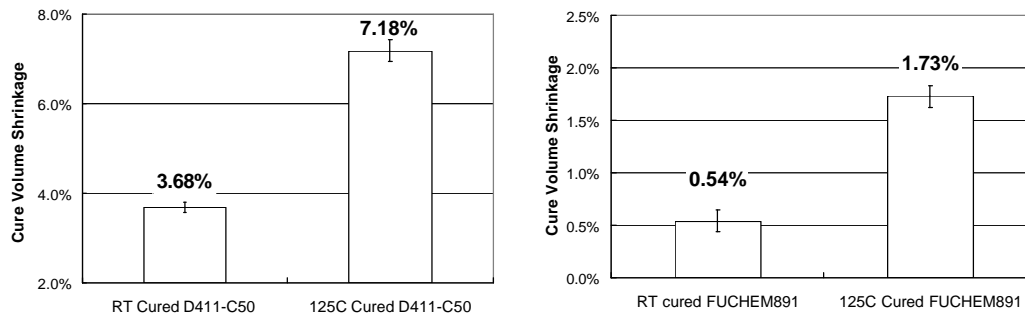
Fig.4 Cure volume shrinkages of the vinyl ester resins measured with lab-made dilatometer



Two cure resin systems were used in this investigation of cure shrinkage influence of the adhesion between carbon fiber and vinyl ester resin. Two different systems were of different initiators: one was CHP-5 and the other one was MEKP. The CHP-5 cure system was based on the manufacturer recommended recipe for D411-C50 and the MEKP cure

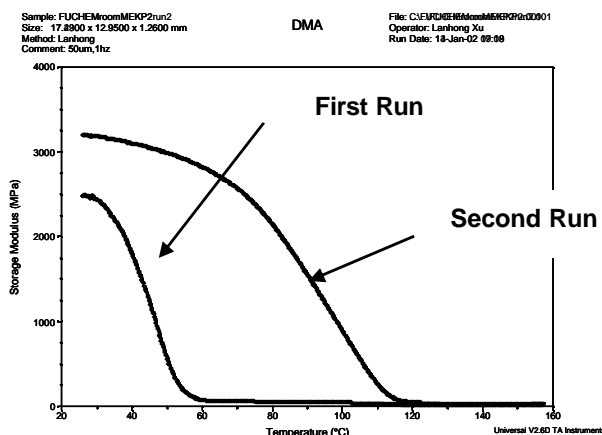
system is based on the manufacturer recommended recipe for Fuchem 891 respectively, shown in the gray columns of Table 1. For the same initiator, the corresponding recipes, the white columns of Table 1, were calculated out from the recommended recipes, the gray columns, based on the density of the carbon-carbon double bond, C=C.

Fig. 5 Influence of Cure Process to the Cure Volume Shrinkage of Vinyl Ester



The results of the cure volume shrinkage measured by the lab-made dilatometer are shown in Fig.4. It has shown that D411-C50 gave a volume shrinkage of 7~8% upon curing. Whereas when Fuchem 891 vinyl ester resin cured with the recommended recipe, 2% of MEKP and 0.1% of CoNap, the cure volume shrinkage was very small, only 1.73% comparing with 8.10% of D411-C50. It is interesting that when Fuchem 891 vinyl ester resins were cured with CHP-5 as initiator using a concentration the same as that of D411-C50 recommended by the manufacturer, the cure volume shrinkage was 5.85%.

Fig. 6 One of the DMTA Measurement for Room Temperature Cured Fuchem 891 V



The cure volume shrinkage of vinyl ester could be changed because of different cure processes. Fig. 5 shows that room temperature cured vinyl esters resulted in lower cure shrinkages. But DMTA tests found that room temperature cured vinyl ester was not fully cured. Fig. 6 illustrates one of the DMTA measurements. A room temperature cured Fuchem 891 sample was put through a temperature cycle from room temperature to 160°C twice at

the ramp of 6°C/minute (cure recipe was recommended by the manufacturer, see Table2). In the second run of the DMTA test, a much higher storage modulus and high glass transition temperature (T_g) resulted indicating that full cure was not achieved in the first DMTA run.

Influence of Cure Volume Shrinkage of Matrix Resin on the Adhesion between Carbon Fiber and Vinyl Ester

The mechanical properties of matrix, which are very important for ITS interfacial shear strength measurements, were tested by nano-indentation as well. During the cure process, it was found that styrene vaporization occurred quickly. The vaporization would be different for those UTS samples made with open sample molds from those ITS sample which

were cut in the middle of the sample bar made with less open molds especially different from the samples measuring cure volume shrinkage with a totally closed lab-made dilatometer. To avoid the influence of styrene vaporization, nano-indentation was used to measure the bulk mechanical properties of the material. It was also found that the bulk elastic moduli measured by nano-indentation were compatible with the tensile moduli measured by UTS. The influence of the cure volume shrinkage of the vinyl ester matrix materials on their bulk moduli were shown in Fig. 7. The bulk moduli of the vinyl ester materials increased with the increase of the cure volume shrinkage of the materials. It might indicate that the cure shrinkage corresponded to a higher crosslink density resulting in an increase of the material properties.

Fig. 7 Influence of vinyl ester cure volume shrinkage on the bulk moduli

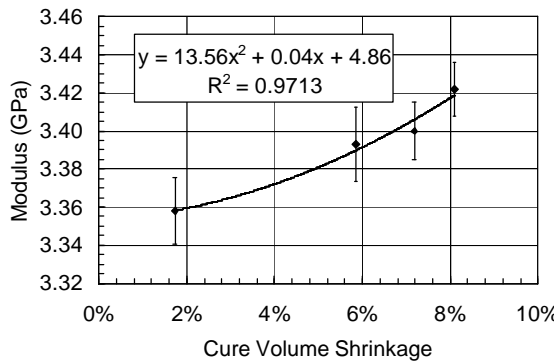
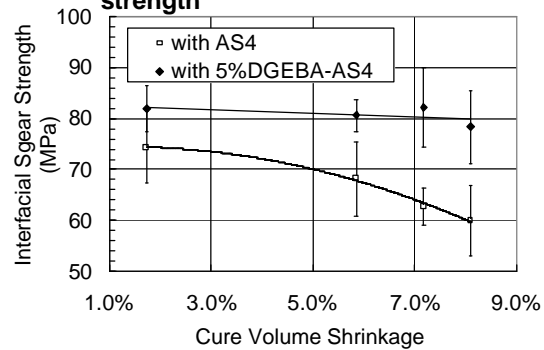


Fig. 8 Influence of vinyl ester cure volume shrinkage on the Interfacial shear strength



Two sets of ITS composite sample were tested by ITS to find out the influence of the cure volume shrinkage of the matrix material on the adhesion between fiber and matrix. One set of composite samples was the vinyl ester having different cure volume shrinkage reinforced by AS4 carbon fiber as received and the other set was the vinyl esters having different cure volume shrinkage reinforced by AS4 carbon fiber with 5% of DGEBA-Jeffamine T-403/Acetone sizing solution. The test results were shown in Fig. 8. The ITS test results were very interesting, for the samples made with AS4 carbon fiber as received, the interfacial shear strength showed a progressive decrease with the cure volume shrinkage of the matrix material, the bigger the cure volume shrinkage the more significant the decrease of the interfacial shear strength. In contrast, for the samples made with carbon fiber with DGEBA-T403 sizing, the value of the interfacial shear strength had little change even for a large cure volume shrinkage of 8.2%. This suggested that the cure volume shrinkage has a negative effect on the adhesion between carbon fiber and vinyl ester resin. And it was also suggested that the sizing material might play a very important role in elimination of the residual stresses caused by the cure volume shrinkage.

Finite Element Analysis of the Residual Stress Caused by Volume Shrinkage

Once the temperature change associated with 1.73% and 7.18% matrix shrinkage was determined the indenter loading the fiber was modeled. The indenter was modeled by a spherical contact entity (*CONTACT_ENTITY) which was given a prescribed displacement. A displacement function defined in three, piecewise linear portions was prescribed. Initially, while the temperature was decreasing the indenter remains fixed. Once the temperature has lowered to the required value, the indenter moved in a bi-linear fashion. The indenter rate for the first half of the loading is reduced to avoid impacting the fiber too harshly.

Fig. 9 Indenter force time history

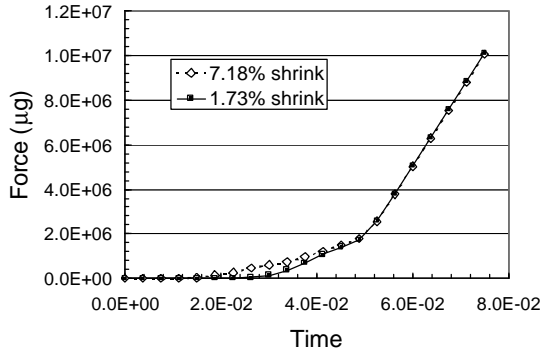


Fig. 10 Von Mises stress for a point in the matrix at the interphase-matrix boundary located approximately 18 mm from the free surface.

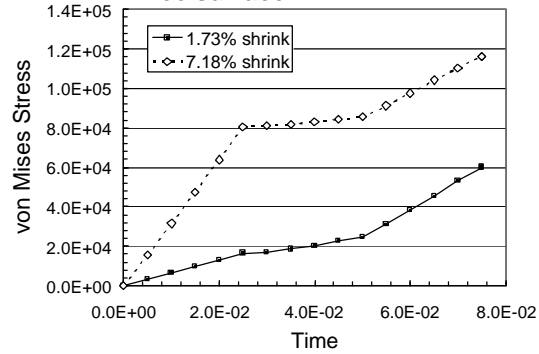
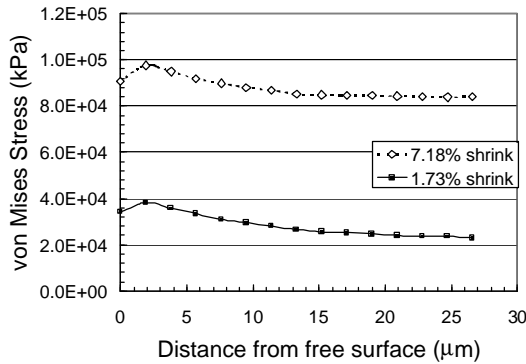


Fig. 11 Von Mises stress distribution for a tup load of 5g as a function of distance from free surface



The nature of the indenter displacement function may be seen by examining the indenter force (Fig. 9). Notice the difference between these two plots between times 0.01 and 0.025 ms where the 7.18 percent case is loading. What is happening is the contraction of the matrix, interphase and fiber is lengthening the RVE enough to contact the tup before it starts to move. Ultimately, the two cases match up during the loading phase of the fiber, so the early difference was ignored.

A good measure of the distortional strain energy (shearing energy) is the von Mises effective stress. Fig. 10 shows the von Mises stress for a matrix element adjacent to the interphase and approximately 18 mm from the free surface in the cases of 1.73% and 7.18% volume shrinkage. (The maximum stress occurs in this vicinity.) Again the nature of the prescribed tup displacement is apparent in the von Mises stress curves. The stress evolutions from the tup loading are similar, but the volume shrinkage has these starting at different value. Thus, the matrix shrinkage has a considerable influence on the matrix stress.

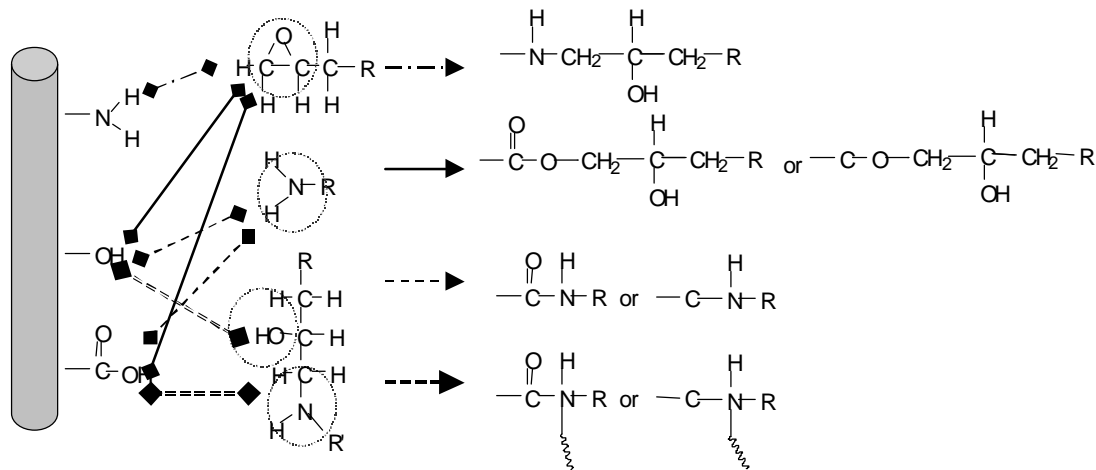
Further comment should be made on the linear loading of the von Mises stress during the volume shrinkage. If a homogeneous, unconstrained material undergoes a temperature change the deformation will be purely dilatary. That means that no shear stress will be generated, hence zero von Mises stress. By the nature of the composite there are constraints in the material and thus distortional strain energy is created when the temperature is lowered. As has been previously alluded to, the maximum stress occurs just below the surface of the composite. Fig. 11 shows the von Mises stress for the matrix adjacent to the interphase as a function of distance from the free surface. Once again, the stress from the matrix/interphase contraction creates a bias in the von Mises stresses.

It appears that the difference in the simulated shrinkage stress is greater than that measured. This disparity is hypothesized to result from the particular RVE selection. By considering near neighbor fibers the matrix would not be allowed to constrict upon the single fiber as much. This would make the differential in the volume shrink stress (before tup loading) to be smaller and thus better model the experimental data.

The Role of Fiber Sizing is Improving Adhesion

The above discussions show that the fiber sizing creates a beneficial interphase between the carbon fiber and vinyl ester resin matrix resulting in a substantial increase in fiber-matrix adhesion regardless of a small or large matrix cure shrinkage. AS4 carbon fibers are surface treated with electrochemical oxidation process that optimizes the adhesion to epoxy. Compared to vinyl ester resin, the amine-cured epoxy sizing material is much more likely to form a chemical bond with the carbon fiber surface. The potential chemical reactions between carbon fiber surface and amine-cured epoxy system are shown in Fig.12. Previous study found that as little as 3% of chemical bonding accounts for a 25% increase in the Interfacial Shear Stress (IFSS) ^[11]

Fig. 12 Potential chemical reactions between carbon fiber surface and epoxy/amine system



The reaction groups are joined by the same kind of lines. The respective products of the reactions are shown at the end of the respective kind of arrows

In addition, Durethane 411 vinyl ester was made from Diglycidyl Ether of Bisphenol A (DGEBA) epoxy. According to the rule of miscibility, two similar materials should be compatible. Actually, further investigation had been carried out to profile the interphase between DGEBA and D411-C50. An interphase specimen was made by merging a DGEBA-T403 plate made from sizing solution into D411-C50 resin mixed with cure catalysts then being cured according to standard process. In Fig.13, test 1 was from DGEBA side to D411-C50, 40 indents, tilt 25°, spacing 20µm and test 2 was 30 indents, tilt 45°, spacing 10µm. Elastic moduli shown in Fig.14, were calculated from the indentation release curve. Distance 0 is about the location of the interphase. It was interesting to see that the value of the moduli in the interphase region was a value between those of the DGEBA and D411 bulk materials. Test 1 gave very consistent moduli on both DGEBA and D411 side, about 3.45GPa and 3.8GPa respectively. The scatter in measured values of test 2 was greater because of the stress field overlap caused by the plastic deformations of the resins after indentation. This was because the spaces between each indentation were too small compared with the tip size of the indenter in test 2. To avoid the overlap of the stress field during test, nano-scratch technique was used.

Fig. 13 Nano-indentation Traces

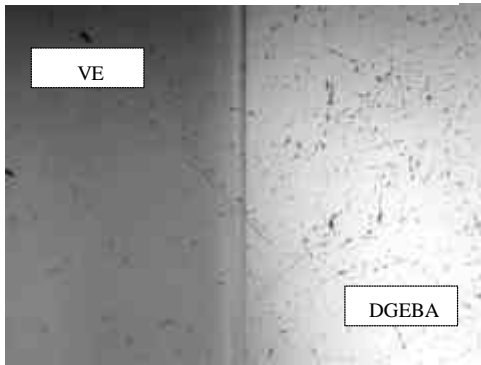


Fig. 14 Nano-indentation Results

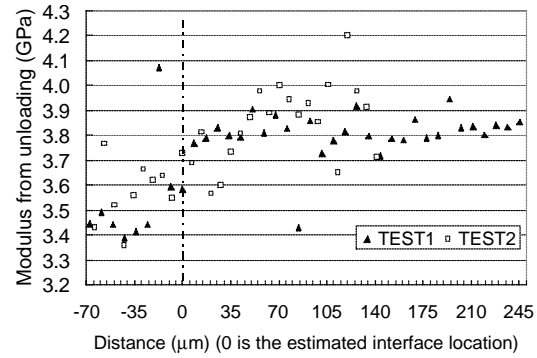


Fig. 15 Nano-Scratch Trace

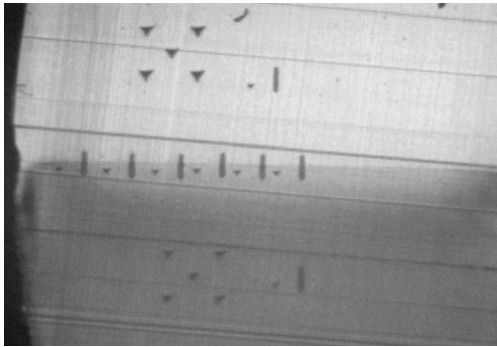
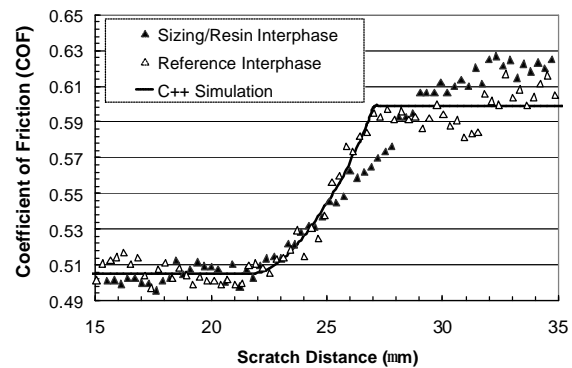


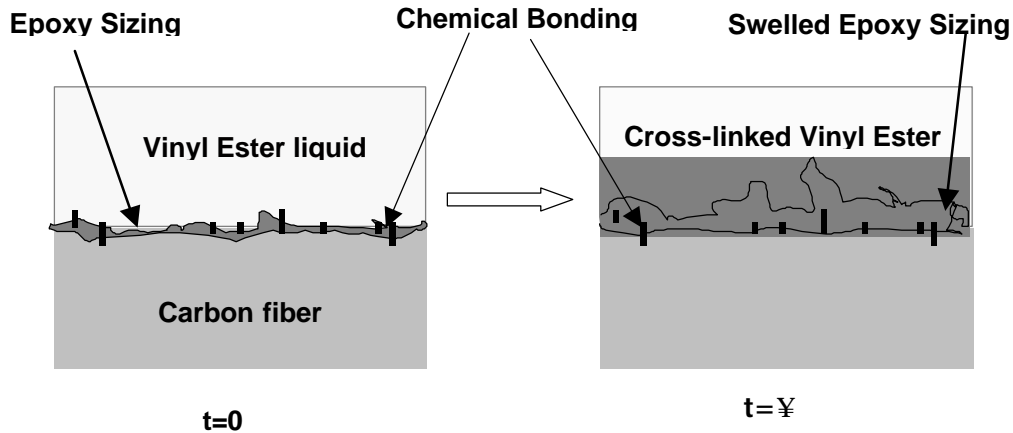
Fig. 16 Nano-Scratch Results



Unlike the nano-indentation test, the nano-scratch test gives continuous information using an index called coefficient of friction (COF) between the material of the indenter and that of the scratched materials. According to the experimental experience in this study that for polymers, when the same diamond scratch tip is used, the harder the material is the lower the COF. A reference interphase sample was made from the sizing subject to drying and oven cure before it was combined with vinyl ester resin. The sample surfaces were microtomed with a diamond knife to avoid the effect of polishing. The scratch trace and scratch data were shown in Fig. 15 and Fig. 16. The scratch distance is 50 μm , see Fig.15, the scratch depth is around 700nm. The scratch data were related to the tip size as mentioned in the Experimental Methods Section and the tip size is related to the depth of scratch. For Fig.16, the line is the representation of the effect of the tip size, the open triangles are the COF of reference interphase which was assumed to have little wideness, the solid triangles are the COF of the sizing /matrix interphase. The COF of the reference interphase was consistent with the C++ simulation line. It was very clear that the width of sizing/matrix interphase was much larger than that of the reference interphase, with a width in the range of 0.5~1.5 μm .

To summarize the discussion above, it could be concluded that the epoxy sizing material provided both a higher degree of probability of chemical bonding to the fiber surface and could be swollen by the vinyl ester monomers. While the sizing material is 'fixed' to the fiber surface by chemical bonding and/or physical bonding, the swollen sizing forms an interpenetrating network which crosslinks with the vinyl ester resin. The sizing material forms an interphase with the matrix network producing a gradient through resin monomer diffusion, resulting in reduced residual stress caused by the cure volume shrinkage at the interphase. This situation is shown schematically in Fig.17 between the two states at $t=0$, where the sized fiber is immersed in the vinyl ester resin and $t=\infty$ the final composite material.

Fig. 17 The swelled sizing material on the interphase between carbon fiber and vinyl ester resin



4. CONCLUSIONS

Cure volume shrinkage of vinyl ester resins are generally determined by the average molecular weight of the vinyl ester monomer and the content of styrene monomer. Normally greater average molecular weight of the vinyl ester monomer and lower the content of styrene monomer result in small cure volume shrinkage as shown in the literature^[4]. The shrinkage is also related to the catalysts of the free radical polymerization and time-temperature process schedule of the process. Different cure temperature and catalysts produce different heats of reaction, cross-link density and degrees of micro-gel formation and/or micro-phase-separation^[12-14].

The cure volume shrinkage of vinyl ester could introduce thermal residual interfacial tensile stress which would decrease interfacial shear strength (IFSS) between fiber and matrix, with increasing shrinkage. The bulk moduli of the vinyl ester resin measured by nano-indentation would increase as the cure volume shrinkage increases. The epoxy sizing on the fiber surface is very important for the relaxation of residual stress caused by cure volume shrinkage. Epoxy-sizing swelling could counteract the cure volume shrinkage of the matrix.

Finite element analyses were very useful for analyzing the interfacial shear stress distribution with matrix shrinkage. The results from finite element analyses were consistent with the experimental results that larger shrinkage produced a greater von Mises effective stress. Experimentation with various RVEs will provide useful information in the future.

DGEBA epoxy sizing provides a beneficial interphase between the carbon fiber and vinyl ester resin. First of all it provided more possibility to form chemical bonding with the composite matrix resin to the surface of carbon fiber reinforcement surface. Second, the epoxy vinyl ester was made from DGEBA epoxy which should be compatible to the DGEBA sizing material. Third styrene monomers can thoroughly penetrate the slightly cross-linked epoxy sizing material and before the matrix is fully cured. This swelling and interpenetration could be very critical for counteracting the matrix volume shrinkage and further more eliminate the residual stress. The optimum sizing thickness is 90~100nm. Nano-indentation test and nano-indentation scratch test are useful techniques for measurement of interphase profile.

5. ACKNOWLEDGEMENT

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