

IMPROVEMENT OF FRACTURE TOUGHNESS AND  
THERMO-MECHANICAL PROPERTIES OF CARBON  
FIBER/EPOXY COMPOSITES USING POLYHEDRAL  
OLIGOMERIC SILSESQUIOXANE (POSS)

By

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2002

Submitted to the Faculty of the  
Graduate College of the  
Oklahoma State University  
in partial fulfillment of  
the requirements for  
the Degree of  
MASTER OF SCIENCE  
December, 2011

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# CHAPTER 1

## INTRODUCTION

### 1.1 Composite Materials

Composite materials have gained popularity (despite their generally high cost) in high-performance products that need to be lightweight, yet strong enough to take harsh loading conditions such for different aerospace applications, marine and automotive industry [1]. The greatest advantage of composite materials is their high strength to weight and stiffness to weight ratio. By choosing an appropriate combination of reinforcement and matrix material, we can produce properties that exactly fit the requirements for a particular structure for a particular purpose.

Composites also have high heat and corrosion resistance which makes them ideal for use in products that are exposed to extreme environments such as chemical storage tanks and spaceship parts. Composite materials are also very durable. Another advantage of composite materials is that they provide design flexibility. Composites can be produced into complex shapes which are generally very difficult to make out of metals [1]. Advanced composite materials consist of new high strength fibers embedded in an epoxy resin matrix. Epoxy resins can be defined as molecules containing more than one epoxide groups. The epoxide groups are also called oxirane or ethoxyline groups. Fig 1.1 shows the chemical structure of an epoxy group.

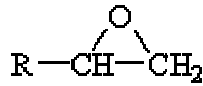


Figure 1.1: Chemical Structure of epoxide or Oxirane Group [2]

These resins are thermosetting polymers. Weight reductions of 20% or better are possible by replacing conventional metal parts with carbon/epoxy composites. Other advantage of carbon epoxy composites over conventional structures is their resistance to damage from cyclic loading (fatigue).

The draw backs associated with using composites is their high manufacturing costs, difficulty of repair and limitations due to lower fracture toughness and impact resistance. To overcome this problems some complementary material such as fiberglass, Kevlar, carbon nanotubes or different nano-additives are added to the basic carbon fiber/epoxy matrix. The added materials are used to obtain specific material characteristics, such as improved fracture toughness, better impact resistance, and better foreign object damage live UV degradation [2].

## 1.2 Toughness of Polymer Matrix Composites

Composites are most susceptible to out of-plane loading, failing in delamination. In recent years, considerable work has been done to improve the fracture toughness, impact resistance and thermo-mechanical properties of carbon fiber epoxy composites. Improvements in the toughness of the matrix has been achieved by adding rigid plastic particles, whisker reinforced interlamination( distributing whiskers in the interlaminar

region during fiber layup process) [3, 4], adding different nano additives [5] as well as interleaving with thermoplastic layers [6]. Also, other efforts to improve the interlaminar strength of laminate composites have met with some success, including 3-D reinforcement and improvements in the toughness of the matrix through nano-additives.

However, the addition of rigid micro-scale fillers to polymers often increases their strength, but decreases their toughness since the fillers or agglomerates may induce stress concentration, which initiates cracks and make them become larger than the critical crack size that causes failure. This is due to rod like features of the additives [7].

Therefore, it would be advantageous to simultaneously toughen and strengthen the polymers. Carbon nano-tubes (CNT) have shown a high potential to improve the mechanical properties of polymers as well as electrical properties [8-10]. DWCNT (double walled CNT) could increase both tensile strength and fracture toughness [11]. However, CNT has not been widely used to improve the mechanical properties because of its high material cost. Another class of nano materials which are used in the improvement of fracture toughness are nanoclays [12]. It is reported that nanoclay could increase the fracture toughness of epoxy by 2.2 and 5.8 times [13]. Researchers also reported more than 35% improvement in fracture toughness due to addition of nanoclay in addition to improved modulus and compressive strength of polymeric systems [14].

Young's modulus and fracture toughness also depends on clay concentration which was determined by using the tensile and 3-point bending method [15]. Several nanoclay additives, which were mixed with DGEBA epoxy resin using a direct blending technique has shown to improve the tensile modulus, tensile strength and fracture toughness of the nano composites [16].

### 1.3 Polyhedral Oligomeric Silsesquioxanes (POSS)

New classes of hybrid organic-inorganic nano particles are being used in recent years to improve the mechanical properties of carbon fiber epoxy composite laminates. One such nano materials are polyhedral oligomeric silsesquioxanes shortly referred to as POSS which can be incorporated into a variety of polymers with useful effects.

A silsesquioxane is a compound with the empirical chemical formula  $\text{RSiO}_{3/2}$  where Si is the element silicon, O is oxygen and R is hydrogen or an alkyl, alkene, aryl, arylene group. Silsesquioxanes have a cage like structure most commonly. POSS Technology is derived from a continually evolving class of compounds closely related to silicones through both composition and nomenclature. POSS chemical technology has two unique features: (1) the chemical composition is a hybrid, intermediate ( $\text{RSiO}_{1.5}$ ) between that of silica ( $\text{SiO}_2$ ) and silicone ( $\text{R}_2\text{SiO}$ ). (2) POSS molecules are physically large with respect to polymer dimensions and nearly equivalent in size to most polymer segments and coils.

POSS molecules are the smallest particles of silica possible. However unlike silica or modified clays, each POSS molecule contains covalently bonded reactive functionalities suitable for polymerization or grafting POSS monomers to polymer chains. Each POSS molecule contains (R) nonreactive organic functionalities for solubility and compatibility of the POSS segments with the various polymer systems and (X) one or more reactive groups suitable for polymerization or grafting. Figure 1.2 shows the basic structure of POSS molecules.

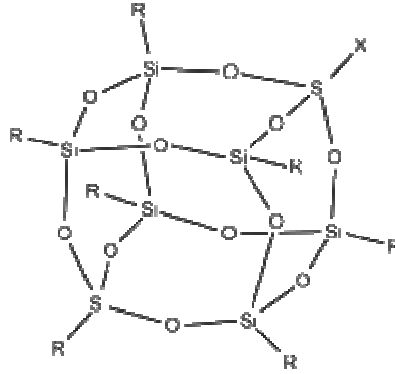


Figure 1.2: Basic Structure of POSS molecules [17]

When mixed with ordinary polymers, POSS they bond to the organic molecules and to one another, forming large chains that cross links through the polymer resulting in a nano structured organic- inorganic hybrid polymer. The POSS chains act like nano scale reinforcing fibers, producing extraordinary gains in mechanical and thermo-mechanical properties.

POSS molecules can interact with epoxy resin in different ways depending on organic substituents. POSS with reactive organic substituents forms covalent bonds. POSS with non-reactive but compatible substituents form polar interaction with the polymer chain.

The polymer systems reinforced with well-defined nano sized inorganic clusters are an important class of polymer nano-composites. Functionalized POSS monomers are covalently bonded to the polymer, leading to reinforcement of the system on molecular level. The resulting nano composite shows improved mechanical properties and higher thermal stability which is determined by POSS-POSS and POSS-polymer interactions [18-20].

Because of their excellent compatibility with common monomers, functionalized POSS molecules can be applied in different modifications. They enhance use temperature, resistance to water and solvent, abrasion resistance, mechanical properties, and resistance to environmental damage [21-28].

Enhancement of mechanical, electrical and thermo-mechanical properties of epoxy based resins has been achieved through the addition of reactive or compatible functionalized POSS and the effect of these additives on curing properties [29-37]. The major drawback with using these POSS nano additives is the formation of POSS aggregates even though the dispersion and homogeneity increases with increasing the reactive functional groups on the POSS [38, 39].

#### **1.4 Polyvinylpyrrolidone (PVP)**

The present study proposes a much simpler way of incorporating these POSS nano-additives into composite laminates using Polyvinylpyrrolidone (PVP)-POSS films or sprays with the PVP acting as a carrier material for the POSS nano- particles. POSS has been added to PVP and shown to improve the  $T_g$  of the PVP polymer [40-43]. But the incorporation of POSS into composite laminates using PVP as a carrier material has not been attempted before.

Polyvinylpyrrolidone (PVP), also called Polyvidone or Povidone, is a water-soluble polymer made from the monomer *N*-vinylpyrrolidone. PVP is soluble in water and other polar solvents. In solution, it has excellent wetting properties and readily forms films. This makes it a good coating or additive to coatings and in solution it

acts as a good dispersion enhancing agent. Figure 1.3 shows the chemical structure of PVP and Figure 1.3 shows a simple schematic for the advantages of PVP.

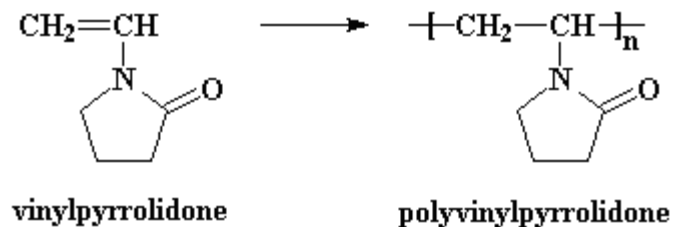


Figure 1.3 Chemical structure of Polyvinylpyrrolidone [44]

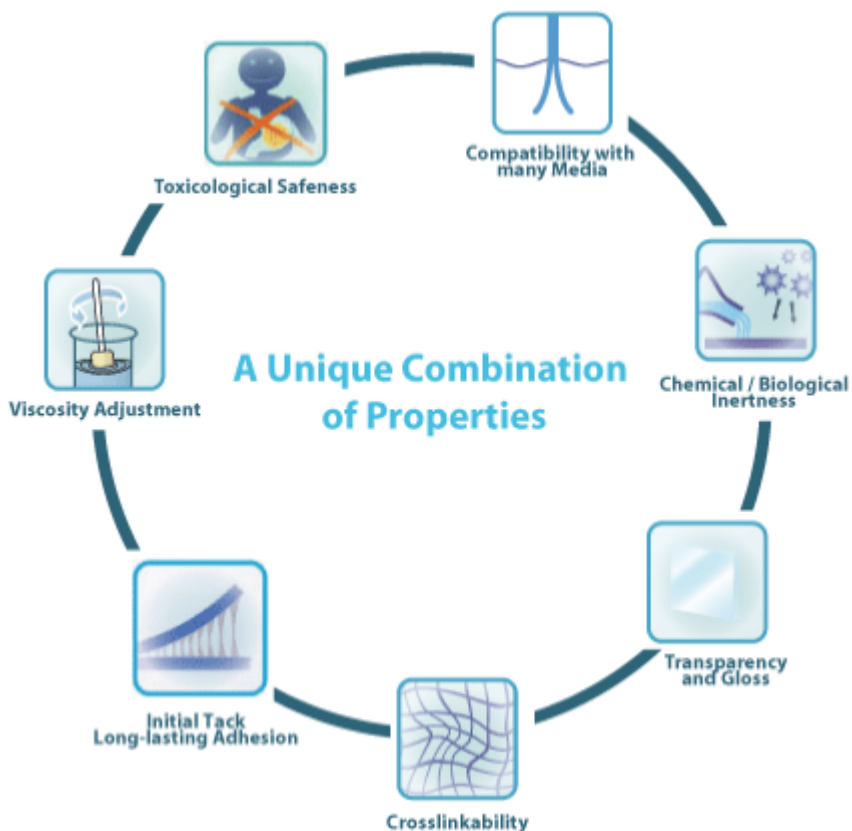


Figure 1.4 An illustration for the Key properties of PVP[44]



**CHAPTER 2**  
**EXPERIMENTAL**

**2.1 Materials**

**2.1.1 Carbon fiber/epoxy prepreg**

Carbon fiber/epoxy prepregs, three types of POSS and PVP K-60 were used in this work. The carbon fiber/epoxy prepregs TORAYCA® C105 carbon fibers of 3K weave and novolac epoxy system and a diamine curing agent (with the company code TEX016) were purchased from TCR composites, Ogden Utah. Table 2.1 shows the mechanical properties of the carbon fibers used. Figure 2.1 shows the chemical structure of novolac epoxy resin.

Table 2.1 mechanical properties of carbon fiber used [45].

Tensile Strength Mpa	Tensile Modulus GPA	Strain	Density g/cm <sup>3</sup>	Filament Diameter μm	CTE °C (x10 <sup>-6</sup> )	Specific Heat Cal/g°C	Thermal Conductivity Cal/cm.s.°C	Electrical Resistivity Ω.cm (x10 <sup>-3</sup> )	Chemical Comp. ppm NA+K.
4,900	230	2.1 %	1.8	7	-0.38	0.18	0.0224	1.6	93 % C  <50

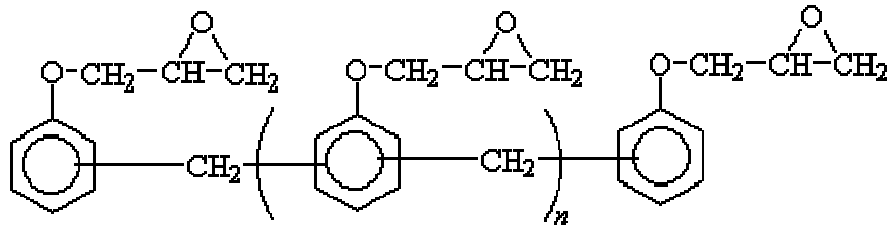


Figure 2.1: Chemical Structure of novolac epoxy [2].

Table 2.2 lists composite properties according to the Toray Carbon Fibers America, Inc. data sheet reported by TCR composites.

Table 2.2: composite properties [45].

Tensile strength	2,550 Mpa
Tensile modulus	135Gpa
Tensile strain	1.7%
Compressive strength	1,470 Mpa
Flexural strength	1,670 Mpa
Flexural modulus	120 GPA
ILSS	900 J/m <sup>2</sup>

The reason behind selecting the carbon fibers pre-impregnated with novolac epoxy was that, or Novolac epoxy resins exhibit greatly improved chemical and heat resistance compared to the much more common Bis A epoxies. They exhibit higher glass transition

temperatures than Bis A epoxies of approximately 25°C. All epoxies will re-harden when the elevated temperatures fall below their transition temperature. However, Novolac epoxies will continue to cure when exposed to temperatures of about 150°C for a few hours. After this 'additional curing' they generally can withstand about 150°C under dry conditions without problems. Regarding their chemical resistance, Bis A epoxies can handle up to 70% sulfuric acid while novolac epoxies can handle up to 98% sulfuric acid [46].

Novolac epoxy resins contain multiple epoxide groups. These multiple epoxide groups allow these resins to achieve high cross-linkability resulting in excellent temperature, chemical and solvent resistance. They are also resistant to humidity compared to ordinary Bis A epoxies [2].

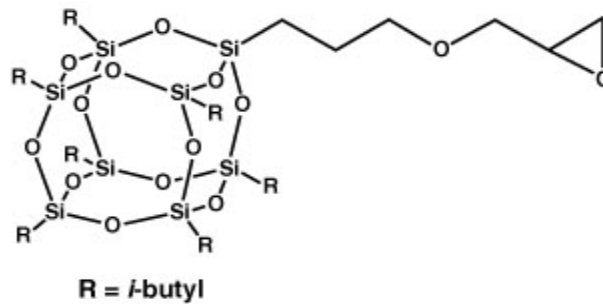
Table 2.3 lists the properties of the neat novolac epoxy according to TCR composites data sheet [45].

Table 2.3: Neat resin properties

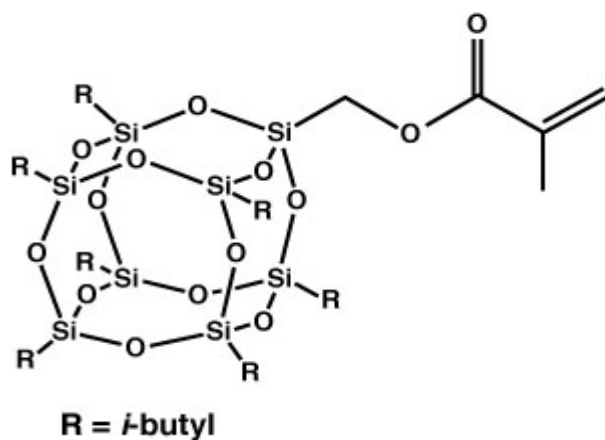
Density (g/cc)	Tg(°C) (from G'' DMA curve)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at break (%)	Tg after 24-Hr water – boil (°C)	Water Absorption (%)
1.208	130	2.83	68.95	5.5	76	3.9

### 2.1.2 Polyhedral Oligomeric Silsesquioxanes (POSS)

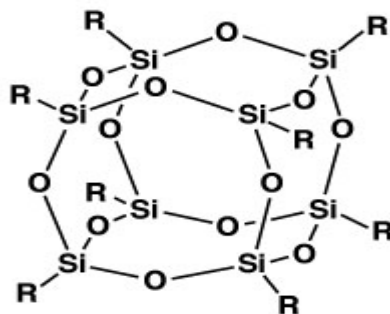
Three types of POSS i) Glycidyl Isobutyl POSS ii) Polyethylene Glycol POSS iii) Methacrylate Isobutyl POSS were purchased from hybrid plastics, Hattiesburg, California. Figure 2.2 shows the types of POSS used in this study.



(a)



(b)



(c)

Figure 2.2: Chemical structures of (a) Glycidyl Isobutyl POSS (b) Methacrylate Isobutyl POSS (c) Polyethylene glycol POSS[47]

The POSS are selected as to compare the effect of the one with epoxide group, with only organic functional groups and non-epoxide reactive group. Glycidyl isobutyl POSS has seven non reactive isobutyl groups and one reactive glycidyl group. It is a good grafting agent and epoxy chain terminator. The polyethylene glycol POSS has eight non-reactive ethylene glycol groups which are compatible with most polymers through covalent bonding and it is a good hydrating and alloying agent. The methacrylate isobutyl POSS has seven non-reactive Isobutyl groups and one highly reactive methacrylate group.

### **2.1.3 Polyvinylpyrrolidone (PVP) and Solvents**

The PVP K-60 was purchased from Sigma Aldrich, Milwaukee, Wisconsin. The solvents used in this work are ethanol (Ethyl alcohol) for dissolving PVP and tetrahydrofuran (THF) for dissolving glycidyl isobutyl POSS and methacrylate POSS. Both solvents were purchased from Sigma-Aldrich, Milwaukee, Wisconsin. Water was used as a solvent for the polyethylene glycol POSS.

### **2.2 Preliminary work and hypothesis**

Delamination is a major failure mode in composite laminates. This drawback has limited their wider applications. Several techniques have been developed to reinforce laminates in the thickness direction, such as stitching and z-pinning. In these techniques, micro stitches or pins are inserted into the laminated composites in the z-direction to provide direct closure forces to the interlaminar crack and enhance the delamination resistance or fracture toughness of these composites [48].

But, this has led to the loss of in-plane properties due to fiber damage, weave distortion and fiber misalignment during the insertion pins and stitches. It is reported that, the tensile and compressive elastic moduli decrease at a linear rate with increasing pin size. The loss in stiffness is due to a reduction to the fiber volume fraction caused by swelling of the composite to give space for the pins, and also distortion of the fibers while forcing the pins into the composite the effect on these pins on the mechanical properties depends on the size of the pins [49].

Recently, improvements of interlaminar fracture toughness with no such sacrifice in other mechanical properties of the composites have been developed, that is the addition of nano-fillers [50-56].

Polyhedral oligomeric silsesquioxane (POSS) will be the focus of this work as a nano-filler. As a preliminary work samples with only PVP additive were made. A film based technique was used to incorporate the PVP thin films in the mid plane of the composite laminates. The resulting sixteen ply composite laminates were tested for fracture toughness and compared with the fracture toughness of the base line carbon fiber/epoxy composite laminates with only epoxy.

PVP was dissolved in ethanol and mechanically (magnetic stirrer) mixed for thirty minutes at 65 °C. Figure 2.3 shows a PVP solution on a magnetic stirrer. The resulting solution was cast into a mold on a tempered glass plate. The solvent (ethanol) was allowed to evaporate at room temperature for 24 hrs and the thin film removed. Figure 2.4 shows a typical PVP film after the solvents have evaporated.



Figure 2.3: PVP/ethanol solution on a magnetic stirrer

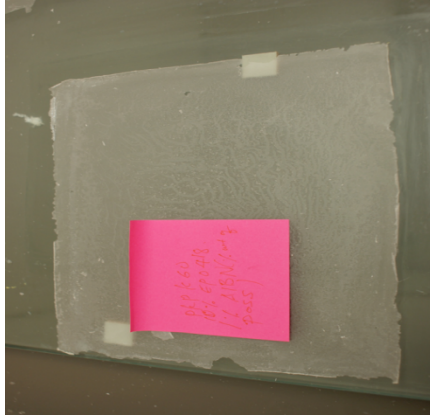


Figure 2.4: A typical PVP film on a tempered glass plate

The composite panels are made by laying up two eight ply layers of the preregs then sandwiching the PVP thin film in the middle. Then, this assembly is put on a hot press under a pressure 74 KPa for one hour at 150°C. The sample is left in the hot press to cool down to room temperature. This is done to avoid any thermal residual stresses in the composite laminates due to rapid cooling. The residual thermal tensile stresses during rapid cooling can significantly reduce the tensile strength of the fiber reinforced composite material [57]. The same samples were made using only preregs to make samples for fracture toughness testing as a base line material.

DCB samples for the mode I inter laminar fracture toughness testing were made according to

ASTM standard D5528-01 [58]. The methods will be discussed in detail in the samples preparation section. DMA samples for the Dual Cantilever Clamp were made of four plies by interleaving PVP thin films between the plies and hot pressing.

Dual Cantilever Beam test for determining the Mode I fracture toughness of the specimens was carried out using INSTRON 5567 testing machine. Also



Dynamic Mechanical analysis was carried out using DMA Q800 from Texas Instruments.

Figures 2.5, 2.6 and 2.7 show the DMA results for the composite laminates.

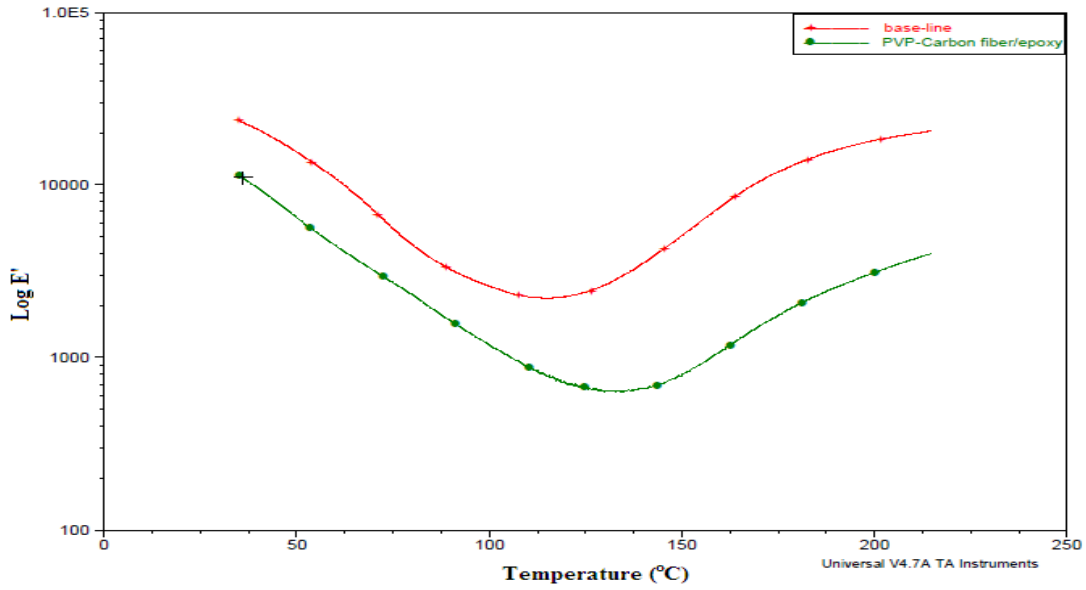


Figure 2.5: Storage Modulus ( $E'$ ) Vs Temp curve

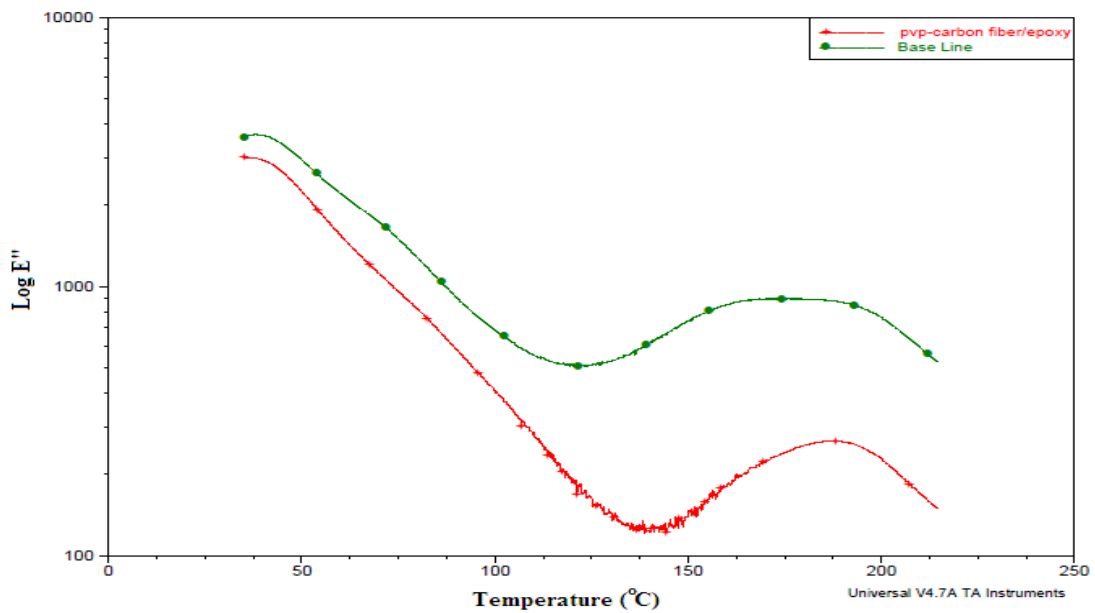


Figure 2.6: Loss Modulus ( $E''$ ) Vs Temperature curve

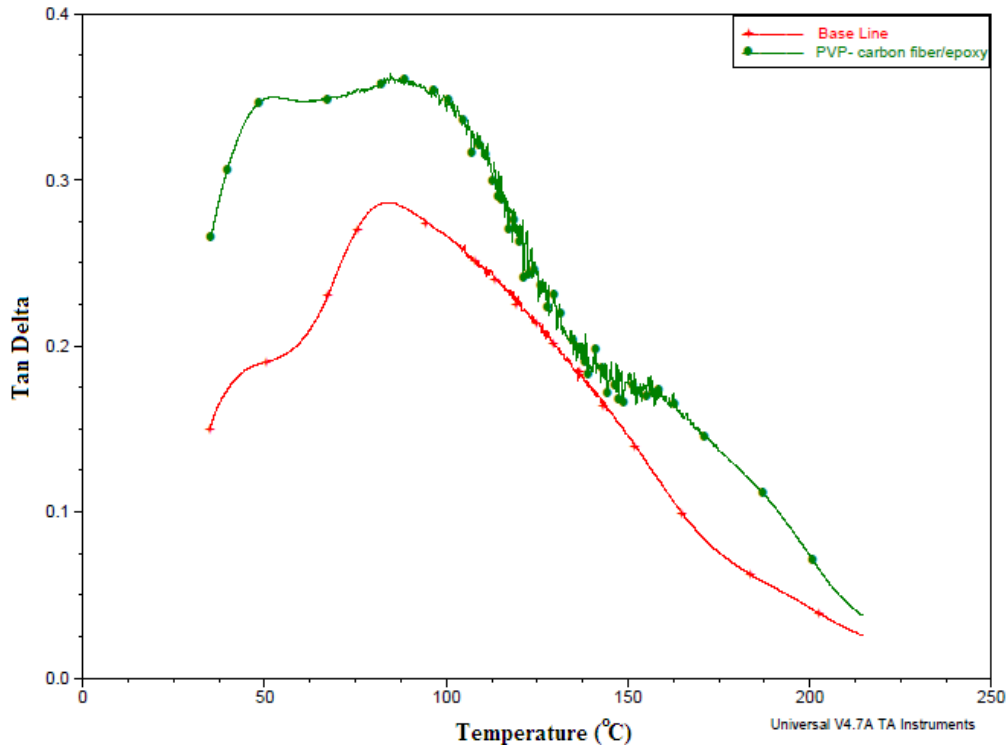


Figure 2.7: Tan  $\delta$  vs. Temperature curve.

The baseline material maintained a higher storage modulus throughout the test temperature range that is 215 °C. The storage modulus decreased by almost 50 percent at 35 °C by the interleaving of the PVP thin films. The percentage reduction in modulus at temperature is higher at higher temperatures. The glass transition which is the peaks of the tan delta curve almost stayed the same except for magnitude, showing higher values in the PVP modified specimens.

The Mode I fracture tests revealed that interleaving of the PVP films in the mid plane of the composite panels greatly reduced the average fracture toughness  $G_{IC}$  of the laminates. The base line laminates lost their mode I fracture toughness by ninety percent by the addition of PVP film into the mid plane of the laminates.

Figure 2.8 shows the load- displacement curve and R-curves of the base line laminates and the PVP modified laminates.

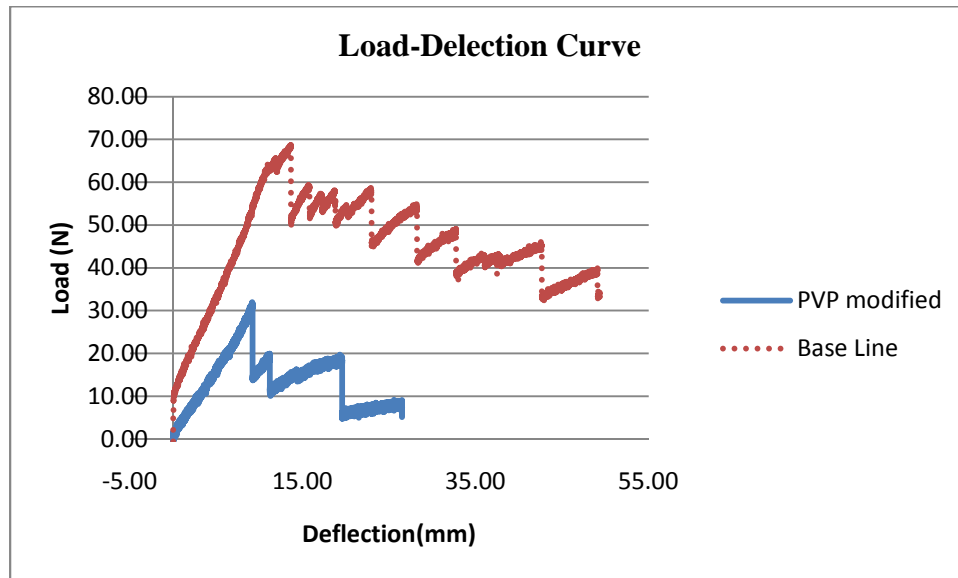


Figure 2.8: Load-deflection curve for the base line and PVP modified Laminates.

This tremendous reduction in the fracture toughness can be explained in terms of the interaction between the epoxy and the PVP thin films. The PVP thin films has a glass transition temperature of 180°C while the optimum curing temperature of the resin system used is 150°C. In the process of making the laminates the optimum curing temperature of the resin was followed and at this temperature the PVP thin films are very stable and unable to react or inter-diffuse with the epoxy resin system. The interfacial diffusion between the PVP and the epoxy is very low at the specified curing temperature because of the poor mobility of the PVP at this temperature. The inter-diffusion between the PVP and the epoxy also depends on the molecular weight of the PVP used. Generally the lower molecular weight PVP has a better diffusion with the epoxy at the curing temperature of the epoxy due to their lower glass transition

temperatures. That is, this PVP has high mobility at lower temperatures than the high molecular weight PVP K-90 [59].

This low mobility in PVP resulted in a very low de-lamination resistance in the resulting PVP-modified laminates. To overcome this problem a spray (paint) technique was developed to incorporate the PVP or PVP-POSS films into the composite laminates and will be discussed in the next section. The following plot shows the delamination resistance (R-Curve) for the base line material and the PVP modified laminates.

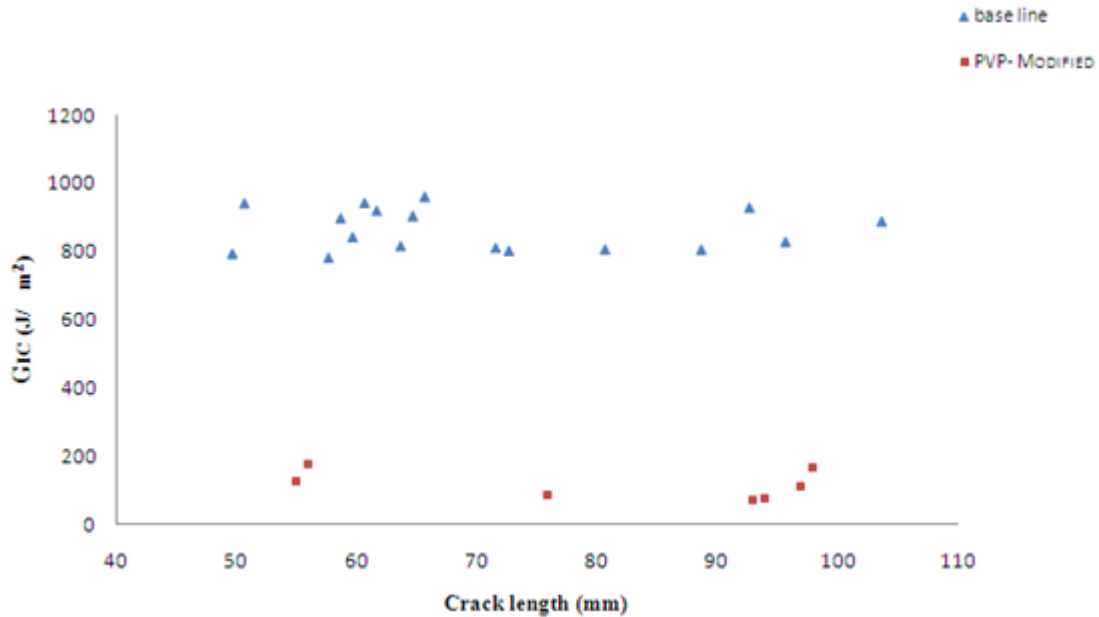


Figure 2.9: Delamination Resistance curve from DCB test of the base laminate and the PVP modified laminate.

## 2.3 Sample preparation

### 2.3.1 DCB Samples

Sixteen layers of 127 mm x 230 mm carbon fiber prepreg pieces were cut from the prepreg roll. These layers were aligned, straightened and pressed together using a

laminating roller. The PVP-POSS solution was prepared. The PVP was dissolved in ethanol and mixed on a magnetic stirrer for thirty minutes at 300 rpm, and then POSS was dissolved in minimal THF and added to the PVP-ethanol solution and stirred for another hour. The time is kept optimal to insure complete dispersion of POSS in PVP and to prevent complete reaction between the PVP and POSS. The three types of POSS were added in 1%, 3%, 5% and 10% weight ratio to PVP in the PVP solution.

This PVP solution was painted or sprayed on the one of the two eight ply halves so that it will be in the mid plane of the resulting composite laminate. Extra care should be taken to make the PVP-POSS layer over the surface of the prepreg. This was done by wiping or brushing of any extra PVP-POSS solution from the surface with a paint brush. After painting the solvents (ethanol and THF) are allowed to evaporate at room temperature from five to six hours.

After the solvents were evaporated a non-adhesive insert (Teflon sheet) with a thickness of  $13\mu\text{m}$  was inserted for crack initiation and the two eight plies are joined and cured in a hot press at a temperature of  $150^{\circ}\text{C}$  and a force of 47 KPa for one hour and as discussed earlier the samples were allowed to cool down to room temperature slowly. The same curing cycle was used for all the PVP-POSS modified samples and the base line.

The samples for the DCB testing were prepared according to ASTM Standard D5528-01. This test method describes the determination of the opening Mode I interlaminar fracture toughness,  $G_{\text{IC}}$ , of continuous fiber-reinforced composite materials using the double cantilever beam (DCB) specimen which is shown in figure below [58].

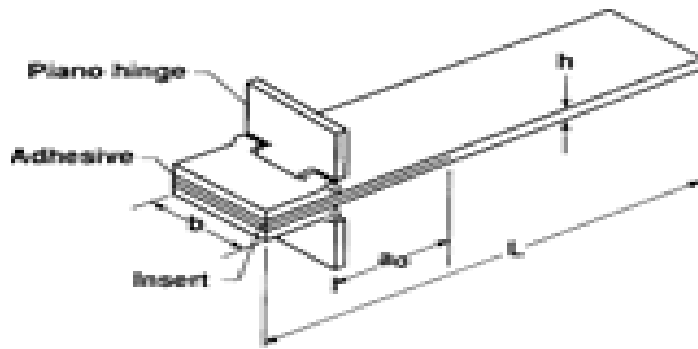


Figure 2.10: A typical DCB sample

Where  $a_0$  — initial delamination length

$B$  — width of DCB specimen.

$L$  — length of DCB specimen.

$h$  — thickness of DCB specimen

The DCB specimen is rectangular and uniform thickness composite specimen containing a Teflon sheet insert on the mid-plane that serve as a delamination or crack initiator. The opening loads are applied to the DCB specimen by means of piano hinges or loading bonded to one end of the specimen with the help of adhesives. According to the standard the specimens were cut from the panels to be dimensions of 125mm long and 25 mm wide with a thickness of 3 mm. And, the initial delamination length was kept at 5 mm from the load line (the hinges) to the end of the Teflon Insert.

### 2.3.2 DMA Samples

Eight layer laminates were made for Dynamic Mechanical Analysis (DMA) testing. The PVP-POSS solutions were made in the same manner as discussed above but they were applied between every layer of the laminate. They are cured in the same manner as the

DCB specimens. The sample dimensions were, 13 mm width, 1.5 mm thick and 60 mm long.

## CHAPTER 3

### CHARACTERIZATION

#### 3.1 Mode I Interlaminar Fracture Toughness

The mode I interlaminar fracture toughness of the composite laminates were Fracture toughness was determined using the double cantilever beam (DCB) test according to ASTM D-5528-01 on universal testing machine (Instron 5567, Norwood, MA). The tests were performed at a cross head speed of 3mm/min. The Mode I interlaminar fracture toughness is calculated using a modified beam theory or compliance calibration method. In this study we made use of the Modified Beam Theory (MBT) Method. The beam theory expression for the strain energy release rate of a perfectly built-in (that is, clamped at the delamination front) double cantilever beam is as follows:

$$G_I = \frac{3P\delta}{2ba} \quad (3.1)$$

Where: P = load

$\delta$  = load point displacement

b = specimen width

a = delamination length.

In practice, this expression will overestimate  $G_I$  because the beam is not perfectly built-in (that is, rotation may occur at the delamination front). One way of correcting for this rotation is to treat the DCB as if it contained a slightly longer delamination,  $a + |\Delta|$ , where  $\Delta$  may be determined by experimentally plotting the cube root of compliance,  $C^{1/3}$ , as a



function of delamination length. The compliance,  $C$ , is the ratio the vertical displacement at the point of load application to the applied load,  $\delta/P$ . The delamination length is measured as observed on the edge of the sample as the crack propagates and the displacements measured simultaneously corresponding to each crack length.

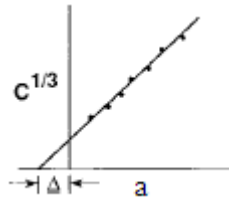


Figure 3.1: Modified beam theory[58]

Then, calculate the Mode I interlaminar fracture toughness,  $G_{IC}$  with the equation:

$$\frac{3P\delta}{2b(a + |\Delta|)} \quad (3.2)$$

The Value of  $G_{IC}$  for all crack lengths and corresponding displacements is calculated and the average taken for all samples.

The figure below shows a DCB specimen while being tested.

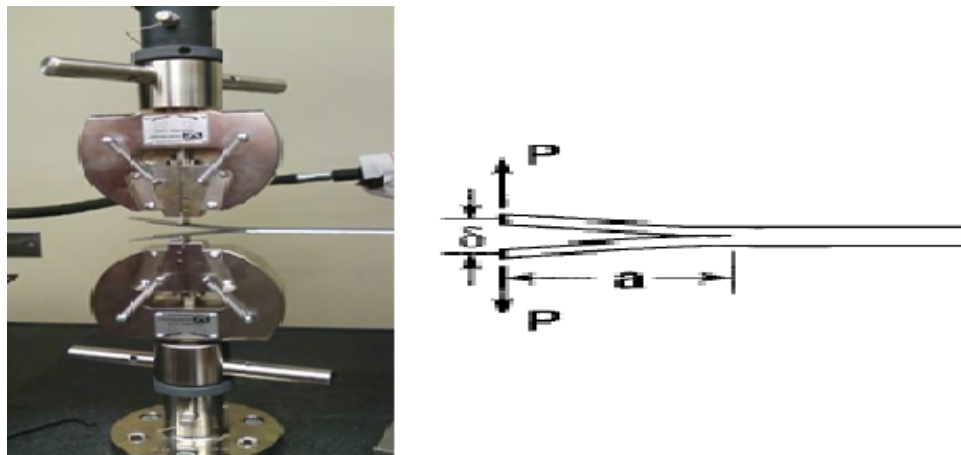


Figure 3.2: A DCB test specimen on a testing machine and schematic of the DCB Specimen.

### 3.2 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was carried out to characterize the thermo-mechanical and damping properties of the composite laminates. Dynamic mechanical testing provides a sensitive test method for determining the low-strain thermo-mechanical characteristics of polymeric materials as a function of frequency, temperature, or time. The Dynamic Mechanical Analyzer (DMA) instrument is used to detect these viscoelastic properties by either applying a small oscillating strain,  $\epsilon$ , to the sample or measuring the resulting stress,  $\sigma$ . Also, by applying a periodic stress and measuring the resulting strain.

The dynamic complex modulus,  $E^*$ , is represented by  $E^* = E' + iE''$  where the real component,  $E'$ , is defined as the elastic storage modulus which is proportional to the energy fully recovered per cycle of deformation; and the imaginary component,  $E''$ , is the loss modulus which is proportional to the net energy dissipated per cycle in the form of heat.

The dynamic storage modulus,  $E' = (\sigma_0/\epsilon_0) \cos \delta$  is the component which is in-phase with the applied strain and  $E'' = (\sigma_0/\epsilon_0) \sin \delta$  is the component which is  $90^\circ$  out-of-phase, where  $\delta$  is the “phase angle” or “phase lag”. The tangent of the phase angle  $\delta$  is then given by  $\tan \delta = E''/E'$  [60]. The storage modulus is related to stiffness, and the loss modulus to damping and energy dissipation. The peak of  $\tan \delta$  vs. temperature curve also indicates the glass transition temperature of a polymer or composite.

In this study a multi frequency-strain procedure at a temperature ramp rate of  $3^\circ\text{C}$  up to  $200^\circ\text{C}$  and amplitude of  $15 \mu\text{m}$  at 1 Hz were used. The upper temperature limit was selected slightly higher than the  $T_g$  of PVP which is  $180^\circ\text{C}$ . The storage modulus, loss

modulus and  $\tan \delta$  were measured using the Dual Cantilever Clamp. (DMA Q800, Texas Instruments).

Figure 3.3 shows a sample mounted on a DMA of the dual cantilever beam test.

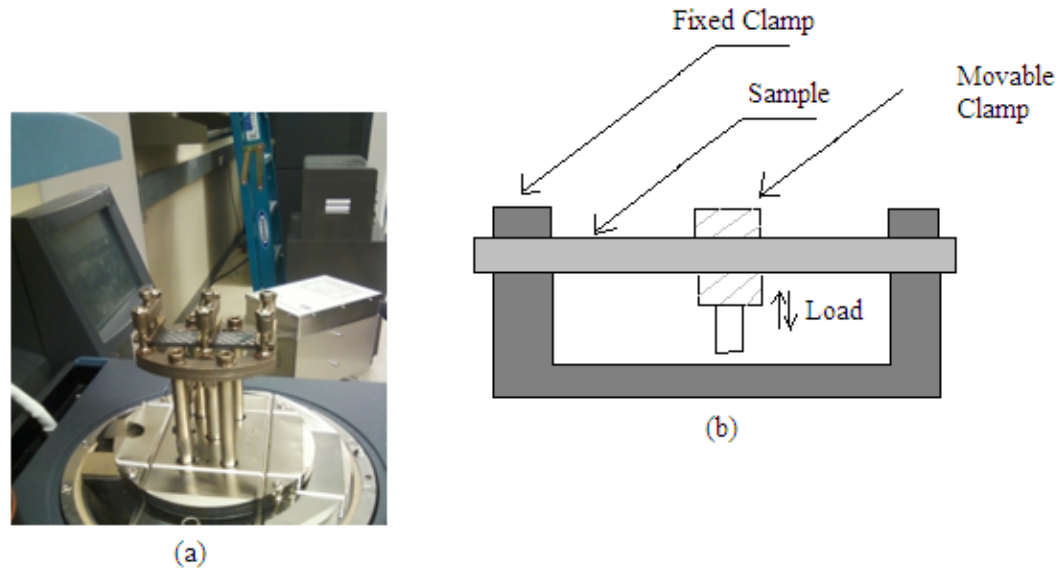


Figure 3.3 (a) Composite laminate specimen on a dual cantilever clamp (b) Schematic of the dual cantilever clamp on a DMA

### 3.3 Scanning Electron Microscopy (SEM)

The fracture surfaces of the laminates from the DCB test were studied using a Scanning electron microscope (Hitachi S-4800 FESEM). The samples were exposed to 20 minutes gold sputtering to get enough material to make the fracture surfaces conductive.

### 3.4 Raman Spectroscopy

The PVP-POSS thin films were studied for Raman Scattering data Using Witec system to understand the changes in chemical bonding due to the addition of POSS to PVP.

### 3.5 Optical microscopy

PVP-POSS thin films were analyzed for optical images to study the dispersion of different POSS percentage loadings in PVP.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Mode I interlaminar fracture toughness

The values of  $G_{IC}$  for different types of mid plane modification i.e. percentage loading of the different types of POSS in PVP of the composite laminates are tabulated below.

Table 4.1  $G_{IC}$  values for different PVP/POSS modifications

%age Loading	baseline $G_{IC}(J/m^2)$	Only PVP $G_{IC}(J/m^2)$	GI POSS $G_{IC}(J/m^2)$	MA POSS $G_{IC}(J/m^2)$	PEG POSS $G_{IC}(J/m^2)$
0%	818.2± 34.3	1084.2±67.1	-	-	-
1%	-	-	1039.2±60.3	1233.8±73.2	1151.8±63.8
3%	-	-	1105.5±40.5	1343.4±58.1	1393.14±29.4
5%	-	-	1579.35±45.5	1079.9±43.6	1095.2±60.4
10%	-	-	1395.3±83.8	1055.6±126	1199.2±33.8

The critical interlaminar fracture toughness as a function of the different POSS types and POSS concentration in the PVP thin films are shown in figure 4.1.

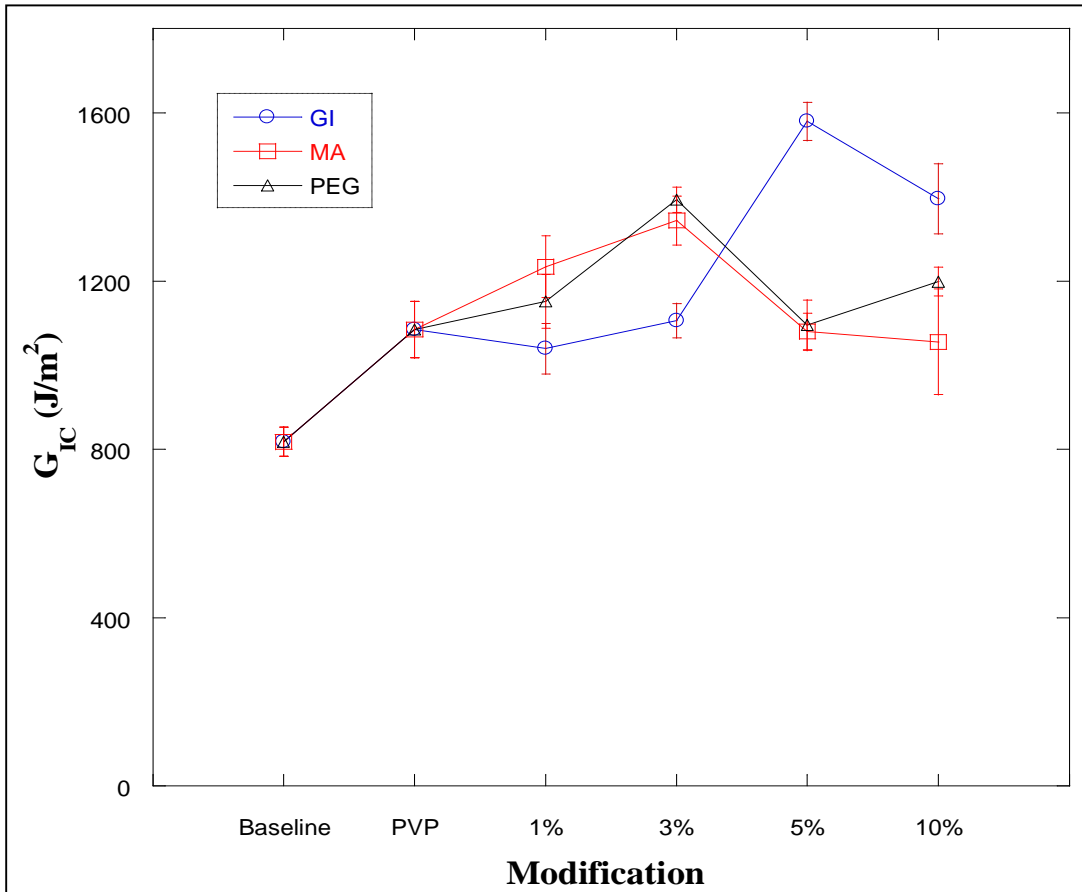


Fig 4.1: Comparison of  $G_{IC}$  values for different modifications of the interlaminar region.

Figure 4.2, 4.3 and 4.4 show the Load-deflection comparisons for base line and GI POSS/PVP modified DCB specimens, base line and MA POSS/PVP modified DCB specimens and base line and PEG POSS/PVP modified DCB specimens respectively.

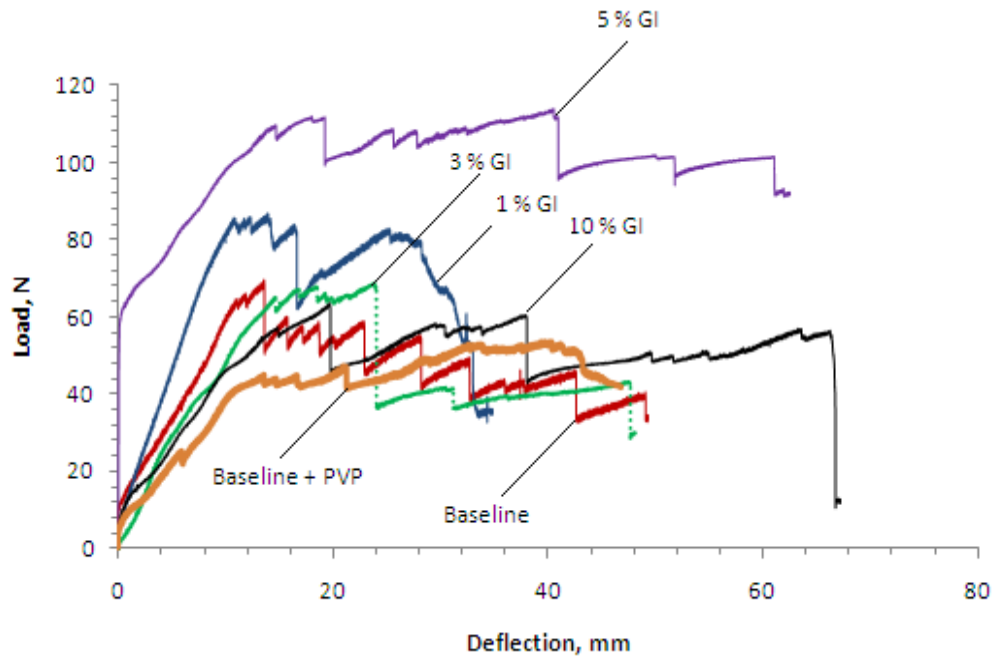


Figure 4.2: Load-deflection curves for GI POSS

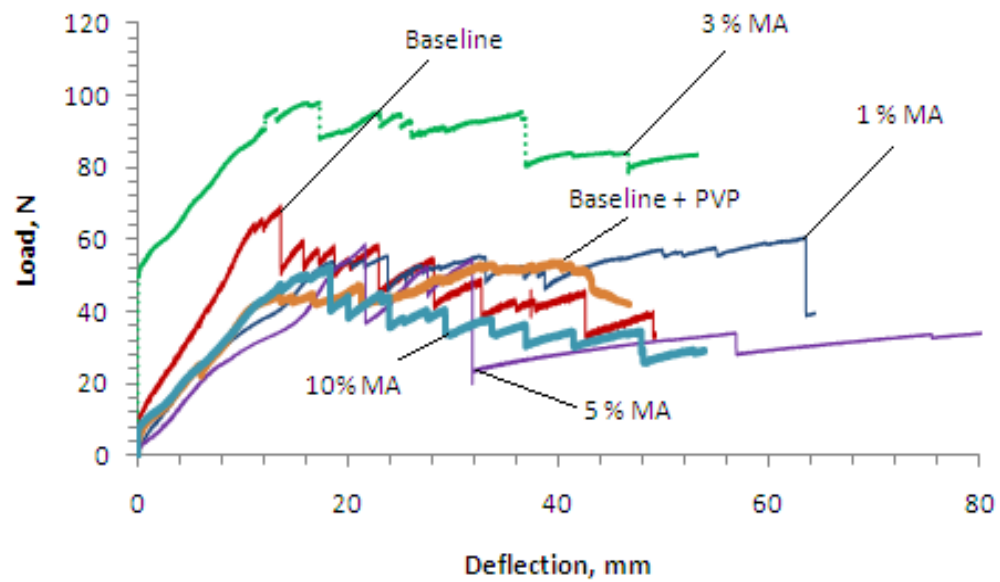


Figure 4.3: Load-deflection curves for MA POSS

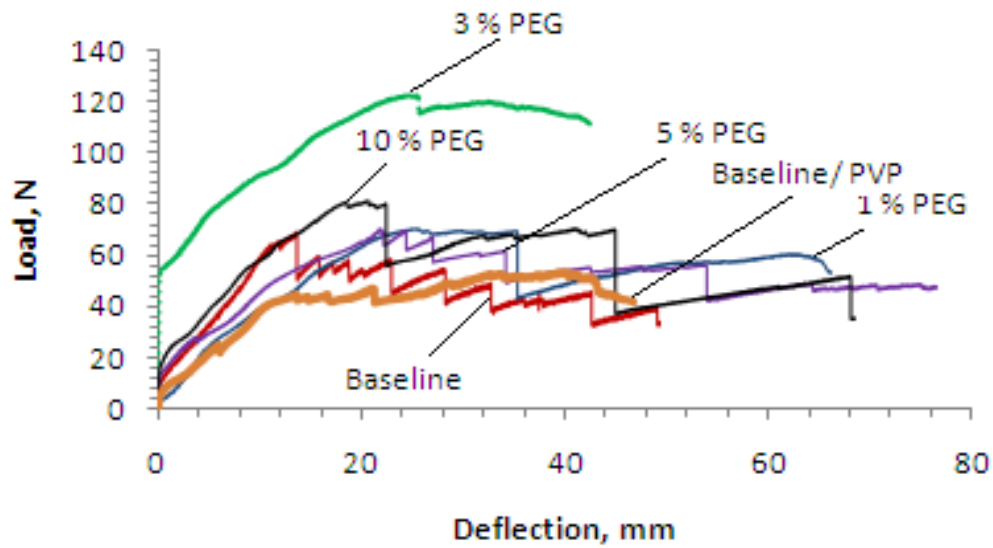


Figure 4.4: Load-deflection curves for PEG POSS

Figure 4.5 shows the percentage increase in fracture energy for modifications with plain PVP and different glycidyl isobutyl percentage loadings in PVP. Specimens with the 5% GI POSS loading in PVP showed a  $G_{IC}$  improvement of 93%. The specimens with a modified with only PVP showed a  $G_{IC}$  improvement of 33%.

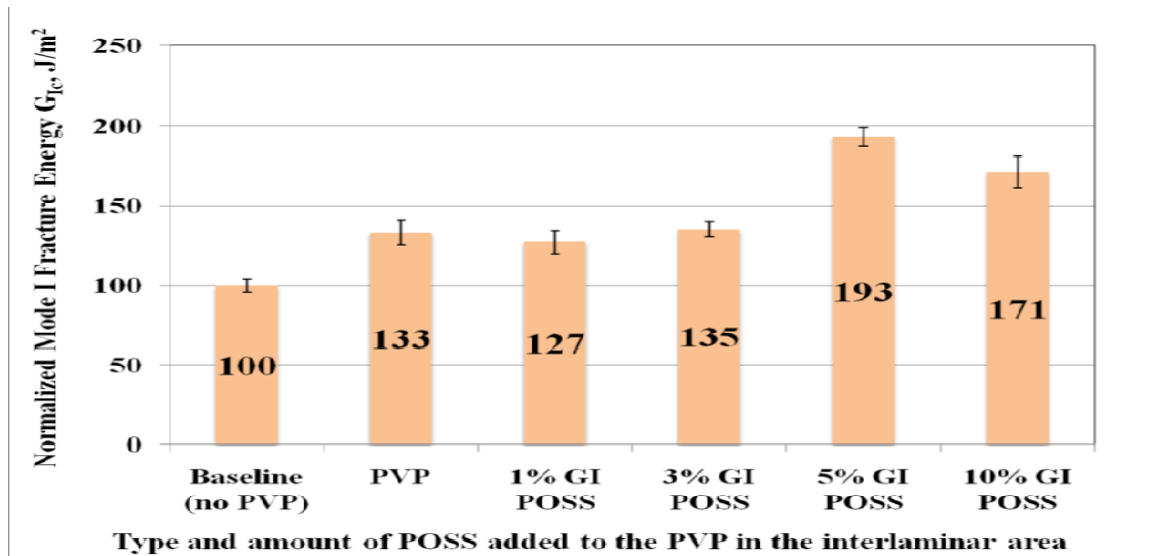


Figure 4.5: Fracture energy comparisons for GI POSS

Figure 4.6 shows variations in fracture energy in specimens modified with methacrylate isobutyl POSS. The specimens with 3% MA POSS loading in PVP showed the highest improvement  $G_{IC}$  of 64%. The improvement in fracture toughness increases with POSS percentage loading in PVP up to 3% and then reduces.

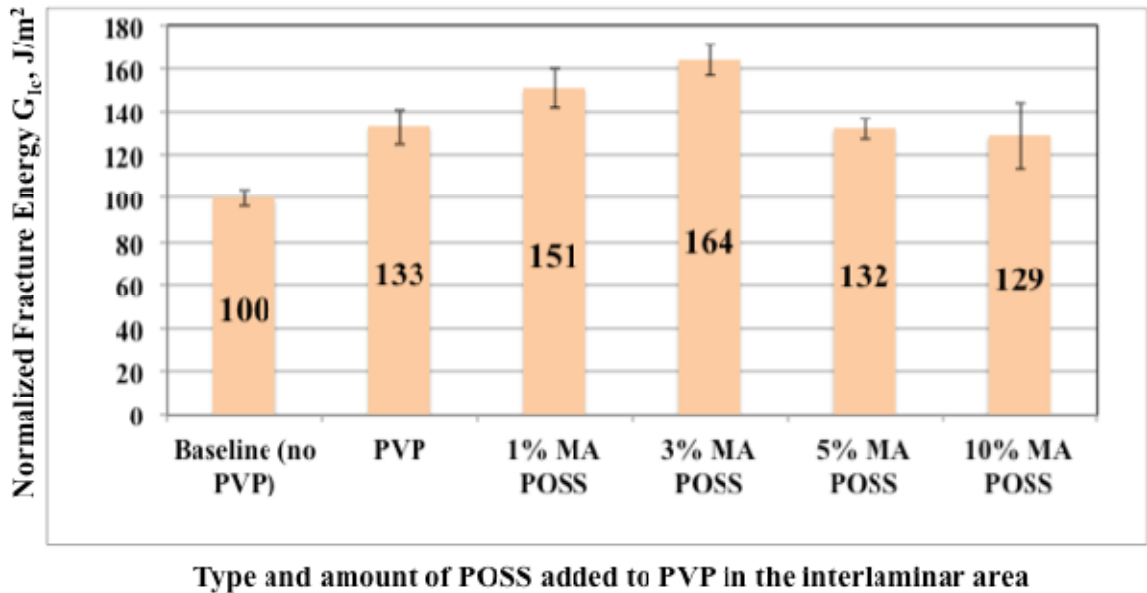


Figure 4.6: Fracture energy comparisons for MA POSS.

Figure 4.7 shows variations in fracture energy in specimens modified with Polyethylene Glycol POSS. The specimens with 3% PEG POSS loading in PVP showed the highest improvement  $G_{IC}$  of 70%. The improvement in fracture toughness increases with POSS percentage loading in PVP up to 3% and then decreases. This is due do the agglomeration of the POSS at higher concentration.



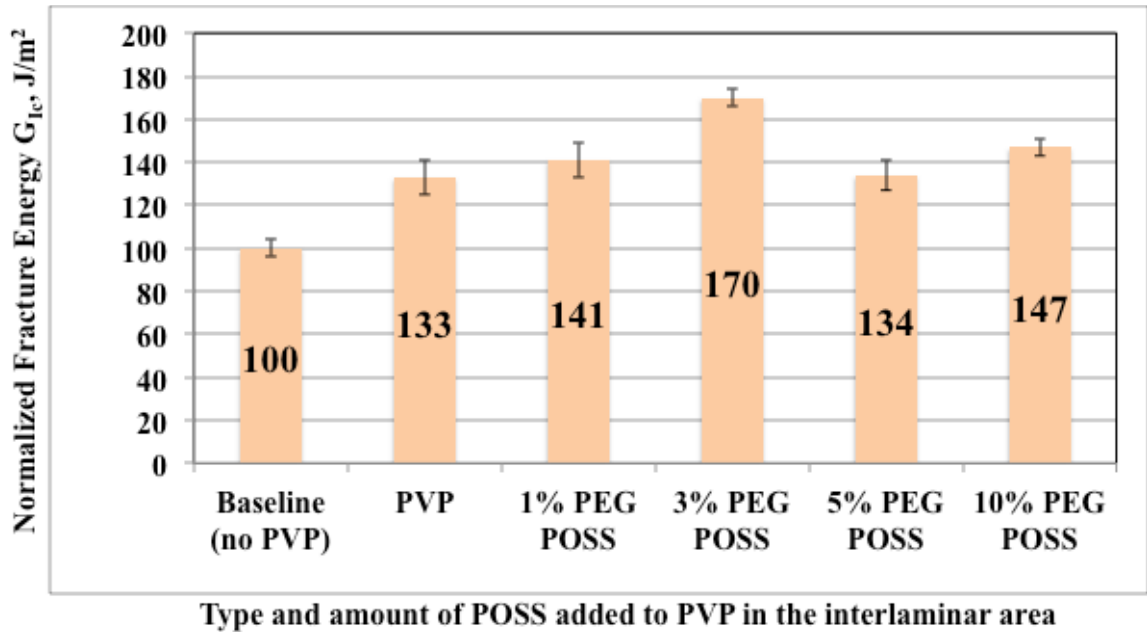


Figure 4.7: Fracture toughness comparisons for PEG POSS

Among the three POSS types used to modify the interlaminar region, the highest  $G_{IC}$  values were exhibited by the composites with GI POSS modification (Figure 4.5), which has one reactive epoxide side group. It was also observed that the range of  $G_{IC}$  values exhibited by the composites modified using up to 3 % MA or PEG POSS were similar. In the case of both MA POSS and PEG POSS, the  $G_{IC}$  values showed a decrease beyond 3% POSS additions. It can be seen that a portion of the fracture energy increase is due to the presence of PVP in the interlaminar area, which would be 33%. The highest percentage improvement of  $G_{IC}$  with the GI, MA and PEG POSS was 93, 64, and 70 percent respectively. Separating the improvement due to PVP alone, it can be deduced that the improvement due to POSS alone is 60, 31 and 37% for the GI, MA and PEG POSS respectively.

The epoxide groups in the GI POSS molecules appear to improve the  $G_{IC}$  to a greater extent than the methacrylate groups and more than the POSS molecules with no reactive groups. Due to the presence of epoxide group in the GI POSS molecule, this particular POSS would essentially behave similar to the epoxy resin as far its interaction with the hardener present in the carbon fiber epoxy prepreg is concerned. This would facilitate GI POSS integrate and cross link well with the prepreg during the composite laminate fabrication process. This result suggests that having a reactive group does improve the  $G_{IC}$ .

#### **4.2 Dynamic Mechanical Analysis (DMA)**

Dynamic mechanical analysis was used to study the changes in the mechanical properties of the composite laminates as a function of temperature. Figure 4.8 shows the variation of storage modulus with temperature for specimens modified with PVP solution containing GI POSS. Similar behavior was also observed in the case of MA and PEG POSS, although the effect was not as significant as the GI POSS. The storage modulus is significantly altered when the interlaminar interface in the laminate composite is modified using PVP solution. Also from Figure 4.8, it is apparent that the storage modulus lost due to the use of PVP solution to modify the interlaminar interface is regained when POSS is added to the interlaminar area through the PVP carrier. The maximum modulus improvement was only 12.55% with the 5% GI POSS/PVP modification. At higher temperatures the baseline specimen maintained higher modulus. This is because at higher temperature the PVP softens and may also phase separate from the matrix while the pure matrix hardens at higher temperatures. Figure 4.9 shows a comparison of storage modules at 35°C and 150°C.

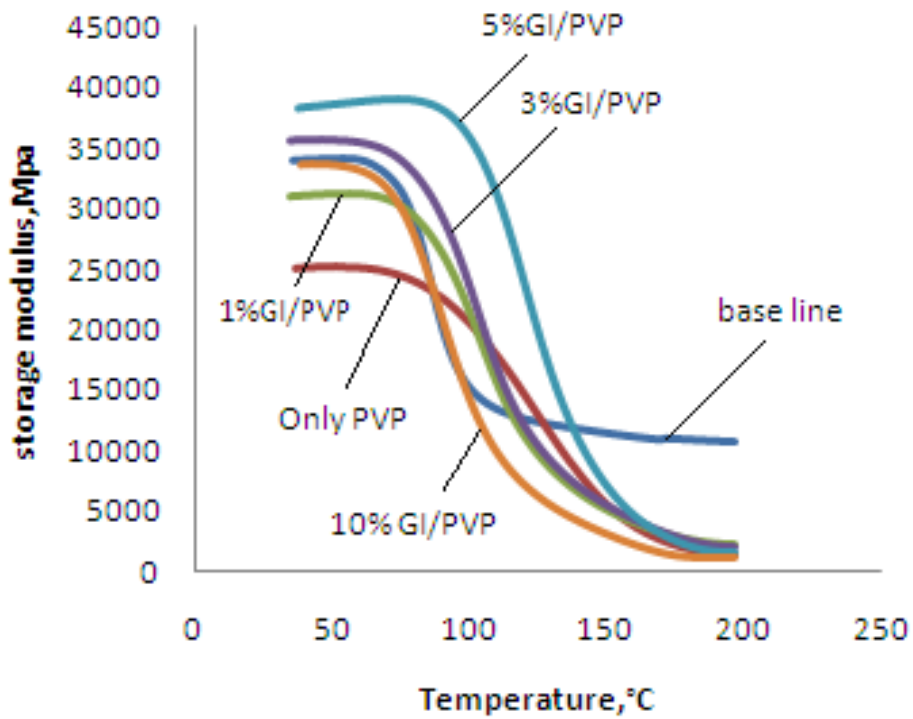


Figure 4.8: Variation of Storage Modulus as a function of Temperature.

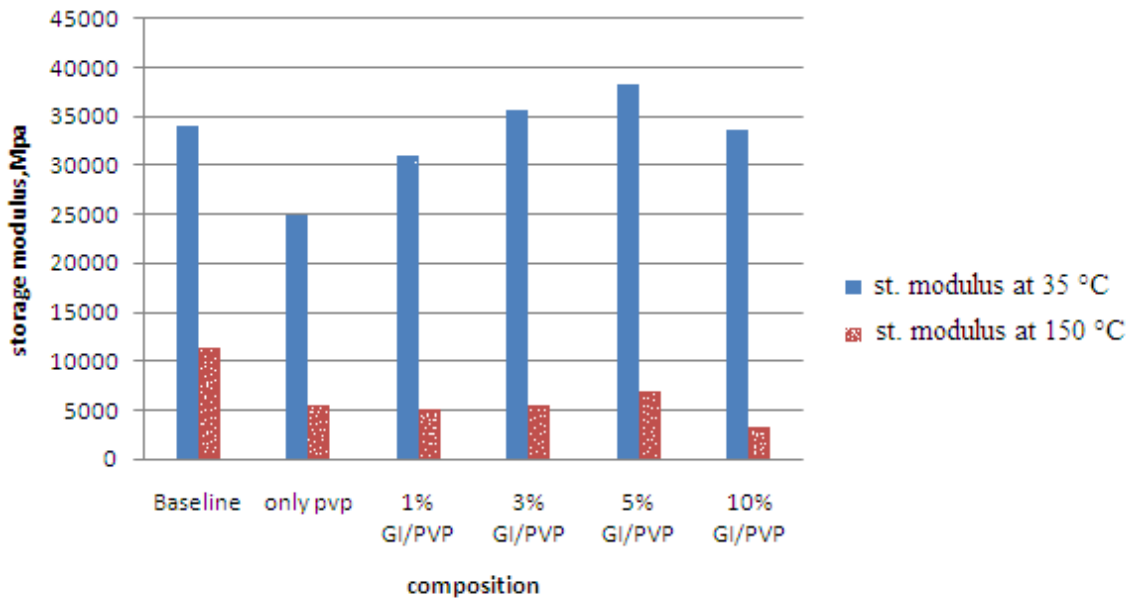


Figure 4.9: Comparison of storage modulus at various temperatures

Figure 4.10 shows variation in glass transition temperature (peak of  $\tan \delta$  vs. temperature curve). Due to the high glass transition temperature of PVP, the PVP layer in the interlaminar region restricts the mobility of the epoxy matrix and a much higher glass transition temperature. It can be observed from figure 4.10 that the peaks of the  $\tan \delta$  vs. temperature curve are very close to each other. The range of the glass transition temperatures for the modified specimens was 138°C to 152°C, the 5% GI POSS/PVP and the pure PVP modified showing the highest values. The glass transition temperature of the baseline specimen was only 89°C. This implies that the percentage loading of POSS in the PVP didn't have a pronounced effect on the glass transition temperature of the composite laminate. Similar results were observed for the MA and PEG POSS.

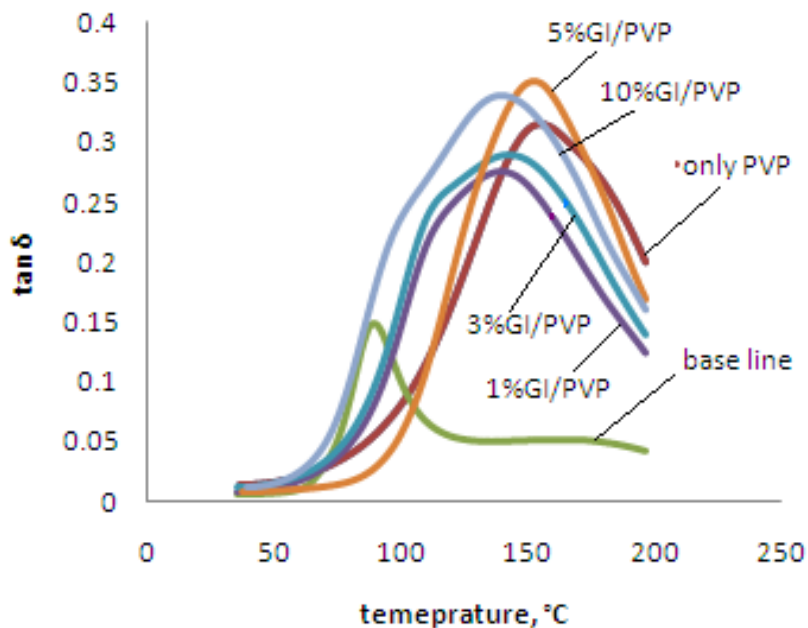


Figure 4.10: Variation of  $\tan \delta$  as a function of temperature.

Figure 4.10 shows comparison for glass transition temperatures. There was a slight reduction in the Tg of the POSS-PVP modified composites as compared to the only PVP

modified composites because POSS acts as a diluent to reduce the self-association interaction of PVP. The interaction between the siloxane of POSS and the dipole carbonyl group of PVP, as well as the physical aggregation of nano scale POSS, result in an increase in Tg of the PVP–POSS composites before reaching the percentage loading where the Tg is maximum and then reducing [61].

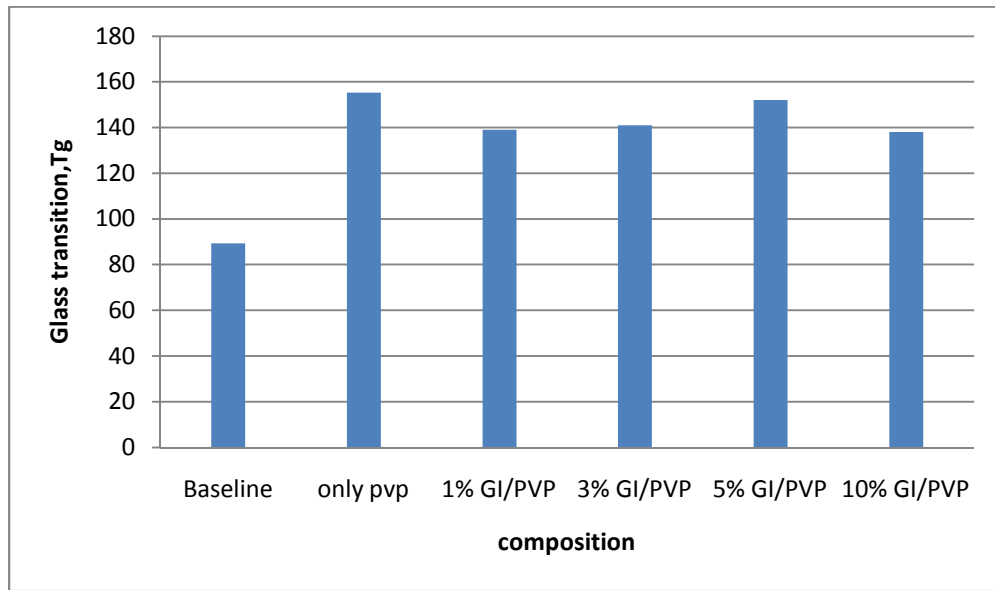


Figure 4.11: comparison of glass transition temperatures

### 4.3 Scanning Electron Microscopy (SEM)

The fractured surfaces were characterized using SEM to understand failure behavior. Figure 4.12 shows SEM images of the fracture surface of unmodified carbon fiber/epoxy laminate. We can see from this figure that the fibers are exposed and there is only a thin layer of resin covering the fibers, this clear appearance of the fiber surface along with ridges left by de-bonded fibers is an indication that the crack progressed across the fiber/matrix interface [62].

Figure 4.13 shows SEM image for fracture surface of a specimen modified with only PVP solution. We can observe from this figure that the fibers are still covered with epoxy/PVP which indicates better matrix fiber bonding due to the addition of PVP. We can also see that there is a considerable crack jumping on the second specimen which resulted in the  $G_{IC}$  improvement of the base line material. The direction of propagation of crack is from right to left.

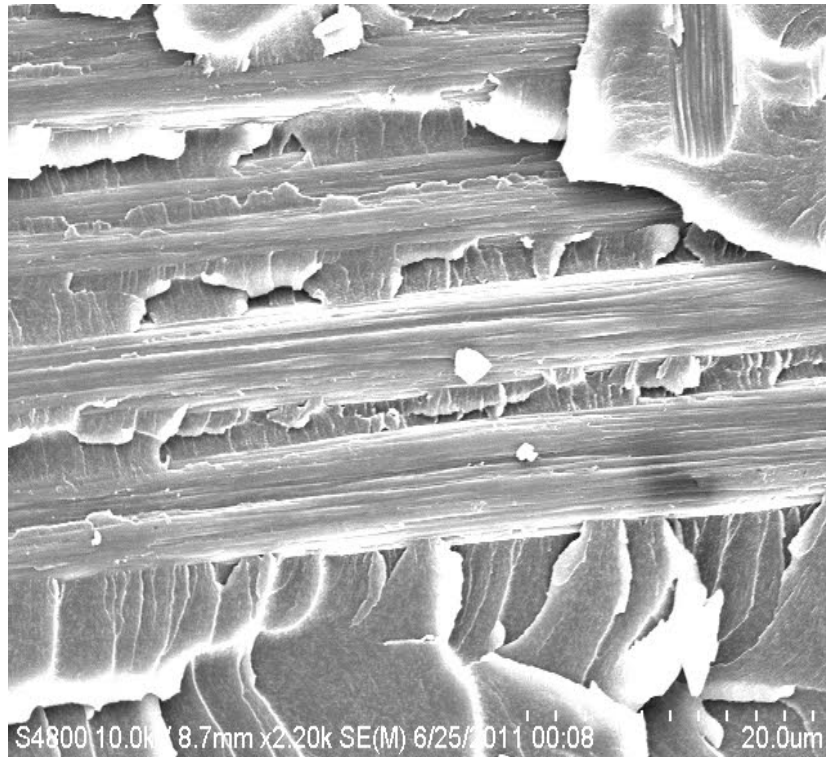


Figure 4.12: SEM image of fracture surface of unmodified carbon fiber/epoxy laminate

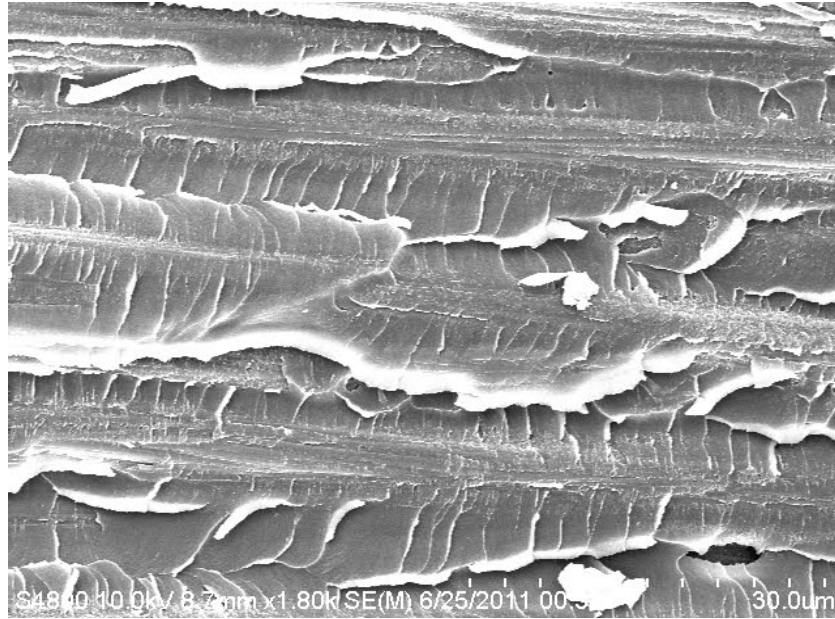


Figure 4.13: SEM images of fracture surface of specimens modified with only PVP solution.

Figures 4.14 a and b show high magnification images of the fracture surface for base line and PVP modified surfaces respectively. we can see porous structures in both specimens resulting from plastic deformation [63].

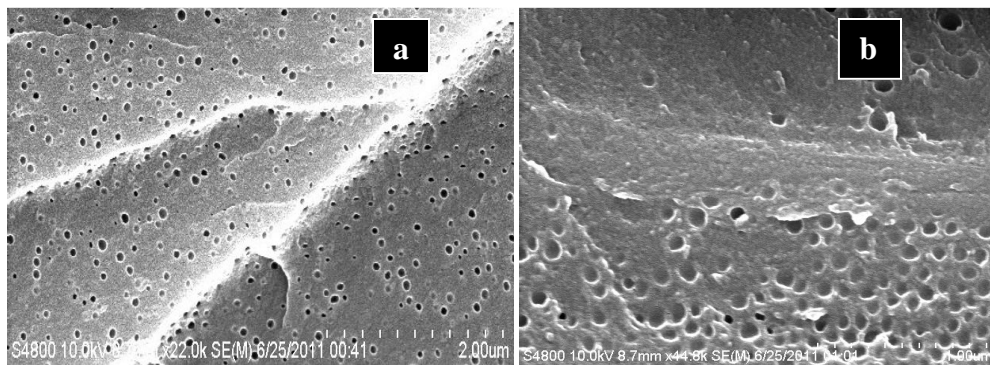


Figure 4.14: SEM images of fracture surfaces of (a) base line specimen (b) PVP modified specimen

Figures 4.15 and 4.16 show SEM images of fracture surface of specimen modified with 1% GI and 5% GI POSS loading in PVP. The 1% POSS loading in PVP didn't show significant change in surface morphology than the specimen modified with only PVP. In figure 4.14 we can see that fracture occurred mainly due to matrix failure and matrix/fiber de-bonding. The river pattern around the matrix is an indication of plastic flow of matrix which leads to higher fracture toughness values [64]. We also can see a good bonding between the fibers and the matrix since the fibers are not exposed fully. This resulted in this specimen's having the highest  $G_{IC}$  improvement among all the modifications.

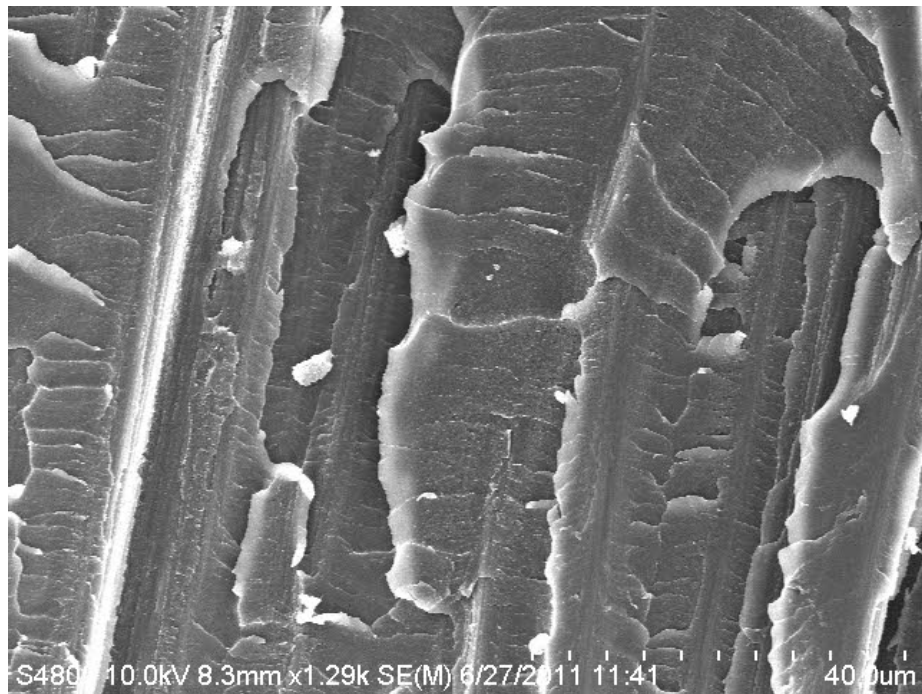


Figure 4.15: SEM images of fracture surface of specimen modified with 1% GI POSS loading in PVP



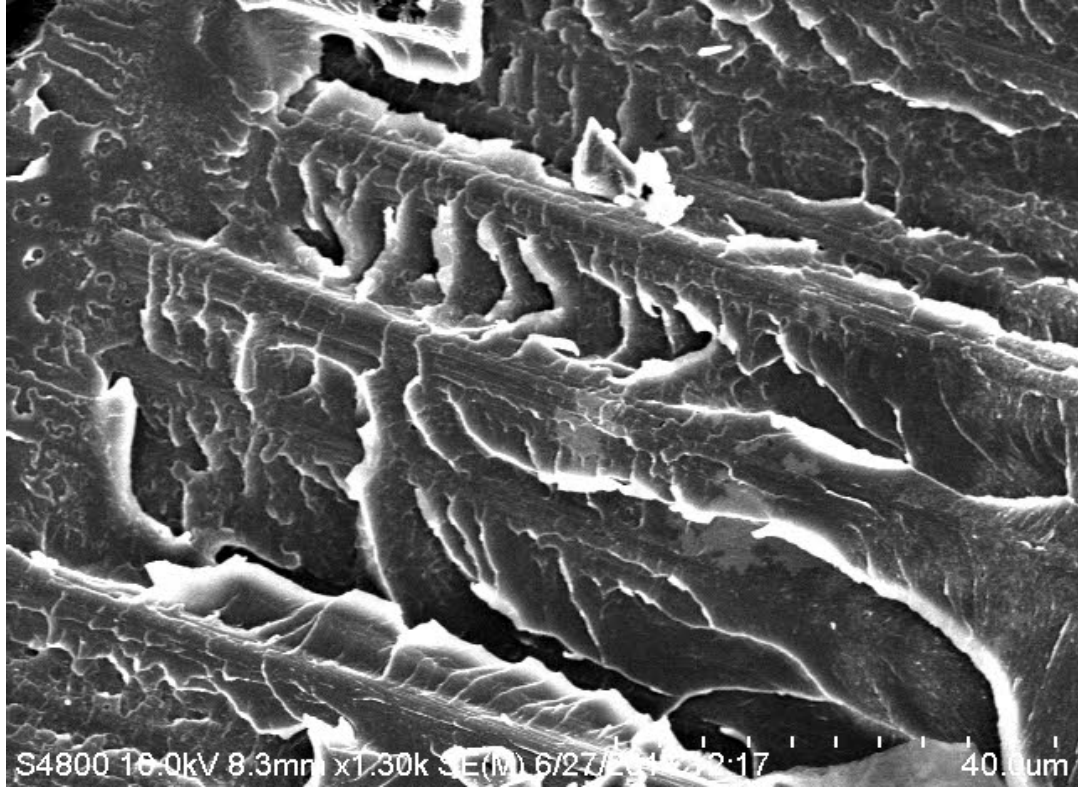


Figure 4.16: SEM images of fracture surface of specimen modified with 5% GI POSS loading in PVP

Figure 4.17 and 4.18 show SEM images of the fracture surfaces of specimens modified with 1% and 3% Methacrylate Isobutyl POSS loading in PVP respectively. From figure 4.17 we can see that the fibers are still covered with layer of PVP/POSS and there is no significant difference than that of the pure PVP or 1% GI POSS/PVP modified specimens.

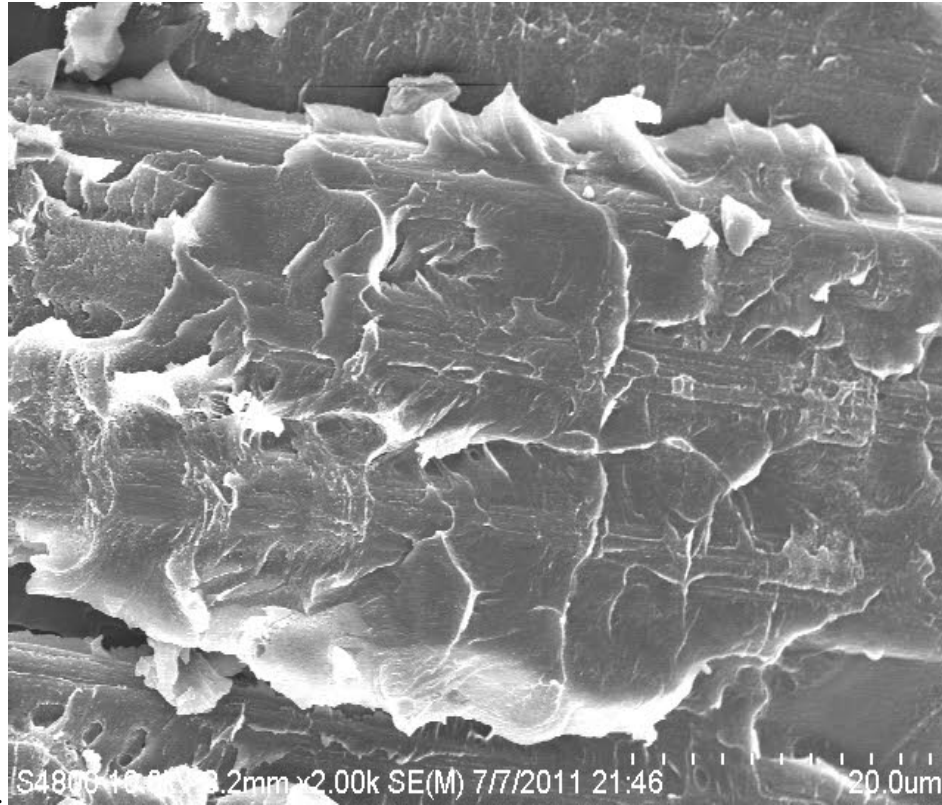


Figure 4.17: Fracture surface of a specimen modified with 1% MA POSS loading in PVP

Figure 4.18 shows fracture surface of a specimen modified with 3% MA POSS loading in PVP. From this figure we can see that there are very sharp fiber fractures indicate good interfacial strength as can be seen on the left top corner of the picture [64]. The hackle markings in the images show pull -out of adjacent fibers [65].

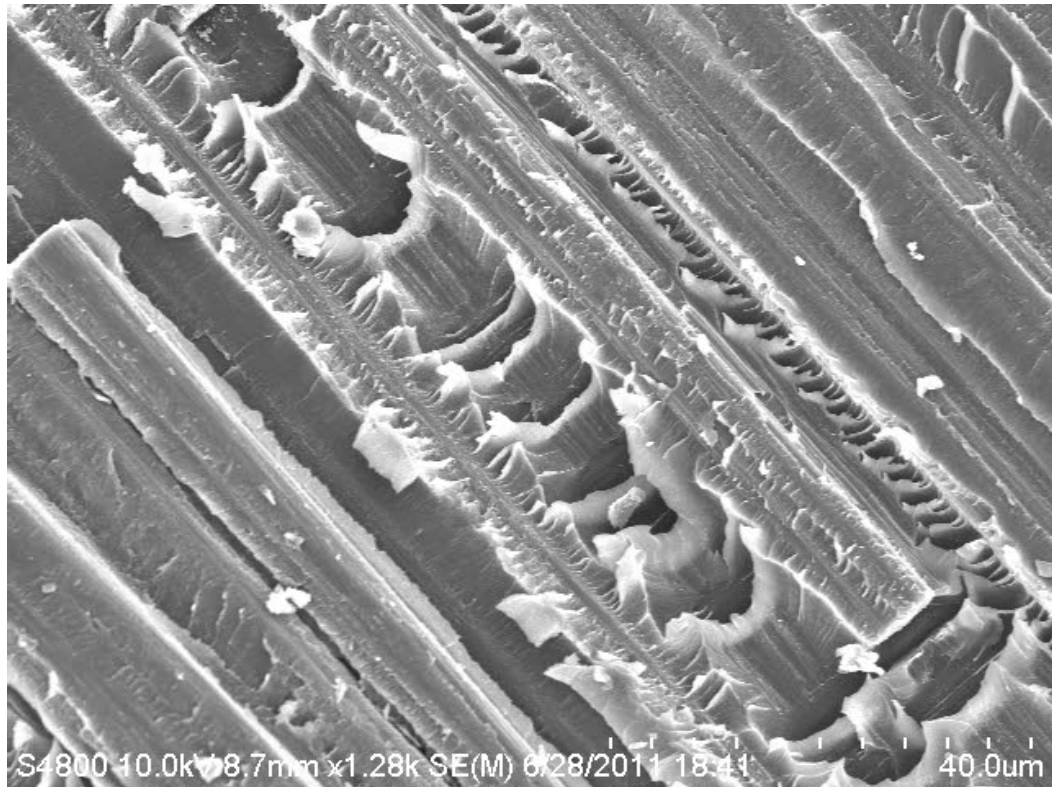


Figure 4.18: Fracture surface of a specimen modified with 3% MA POSS loading in PVP.

Figures 4.19 and 4.20 show SEM images of the fracture surfaces of specimens modified with 1% and 3% PEG POSS loading in PVP. In the 1% PEG POSS/PVP modified sample we observe fiber pull outs and hackle markings. Figure 4.19 also shows the failure is complete fiber matrix de-bonding with some plastic failure in the matrix. The 3% PEG/PVP modified specimen shows a more stable fracture surface, shows greater ductility with the resin being drawn considerably locally. The fibers are considerably covered in resin showing good fiber-matrix bonding.

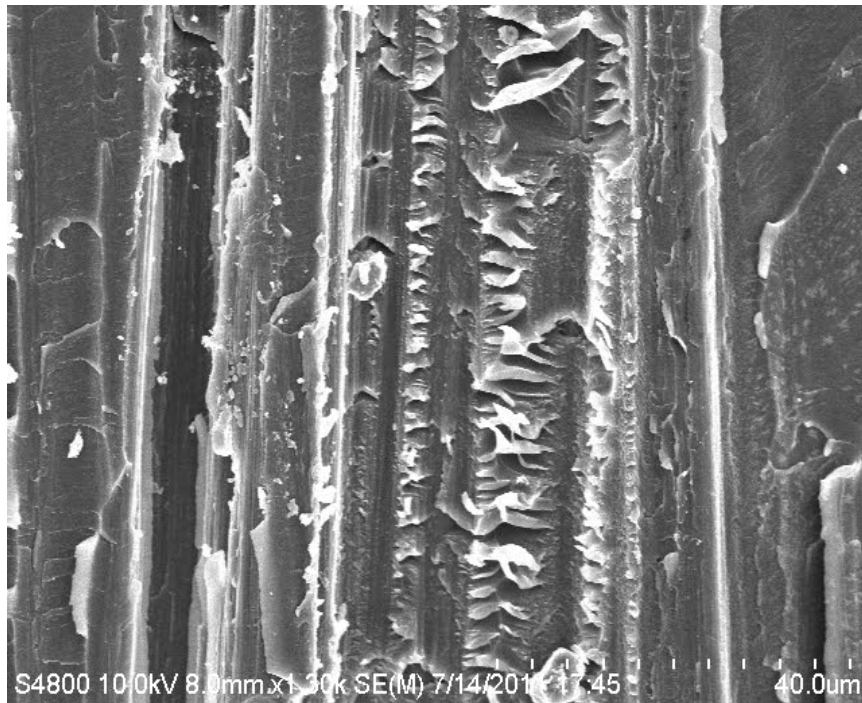


Figure 4.19: Fracture surface of a specimen modified with 1% PEG POSS loading in PVP.

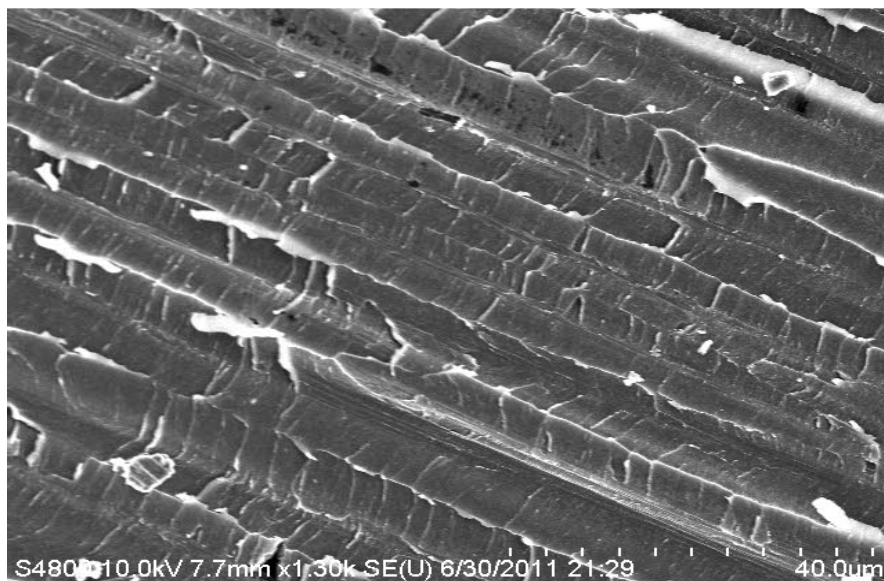


Figure 4.20: Fracture surface of a specimen modified with 3% PEG POSS loading in PVP.

#### 4.4 Raman Spectroscopy

Raman spectroscopy was carried out to characterize the changes in chemical bonding and interaction between PVP and the three types of POSS used. Using Witec system, Raman scattering data was measured from these PVP/POSS films. Figures 4.21, 4.22 and 4.23 shows Raman spectra obtained from different GI POSS/PVP, MA POSS PVP AND PEG POSS/PVP thin films. Raman spectra obtained from all of the thin films and pure POSS show a shoulder at  $2873\text{ cm}^{-1}$ . This shoulder can be attributed to  $-\text{CH}=\text{CH}_2$  group CH vibrations present in the PVP. No shifts in shoulders (wave number) with increasing POSS loading in all the three types of POSS. Also, shoulders seen in the pure POSS samples are also observed in the PVP/POSS films without any shift in wave numbers. We can conclude that there was no noticeable change in bond nature of the PVP at the specified concentrations and POSS types.

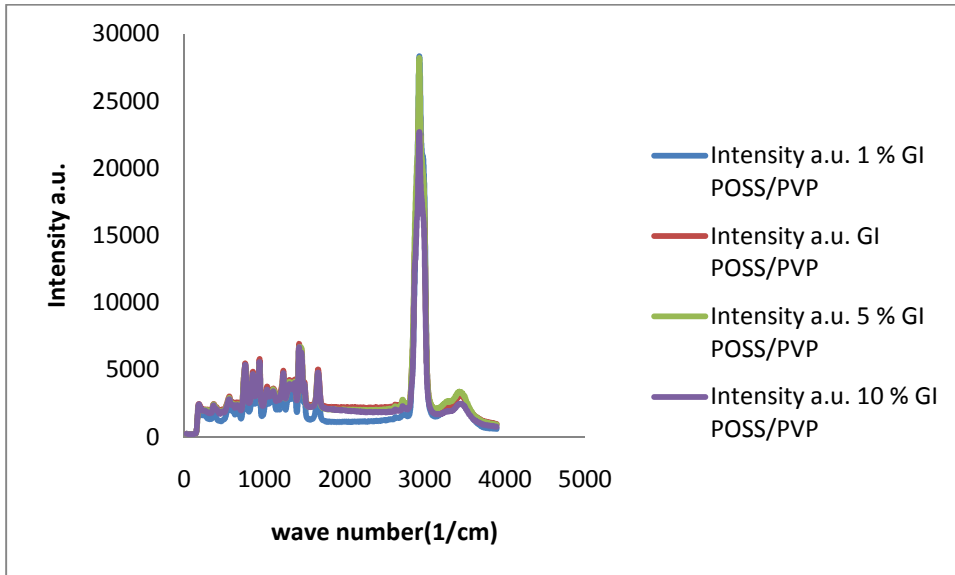


Figure 4.21: Raman spectra of different GI POSS/PVP films

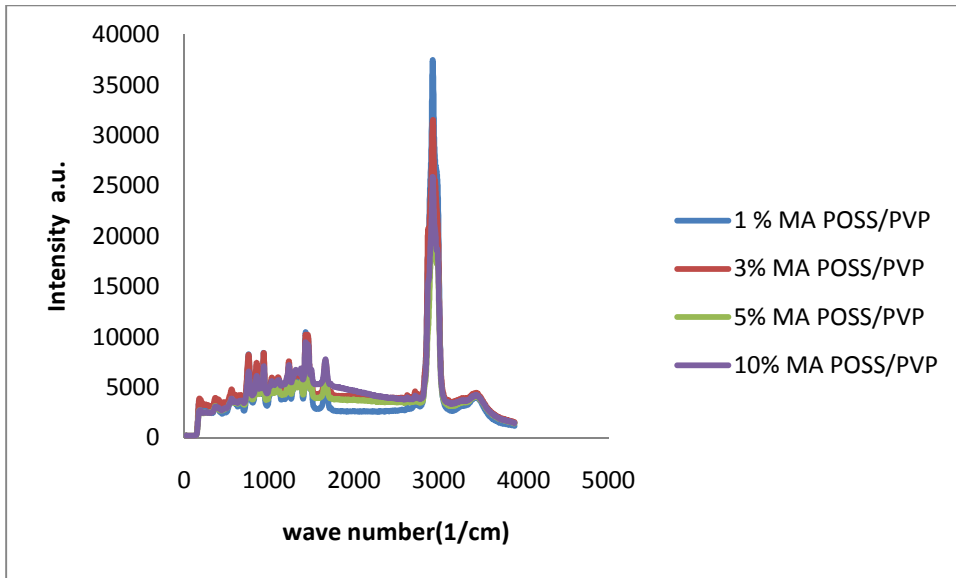


Figure 4.22: Raman spectra of different MA POSS/PVP films

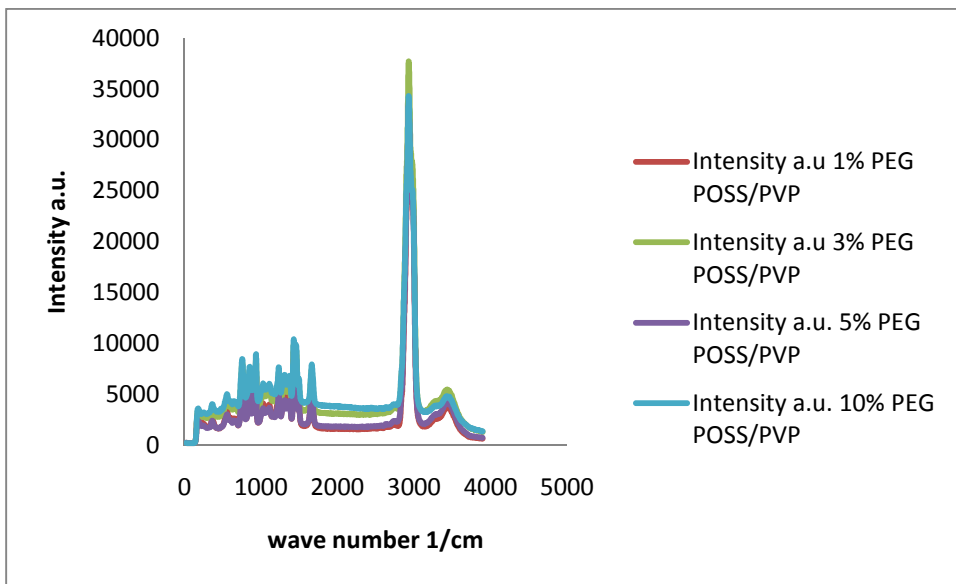


Figure 4.23: Raman spectrum of different PEG POSS PVP thin films

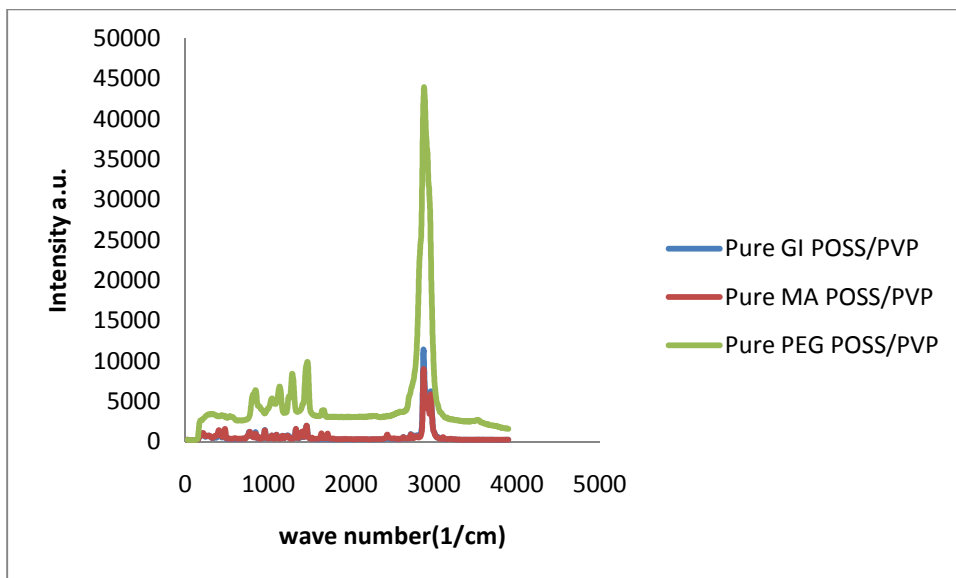
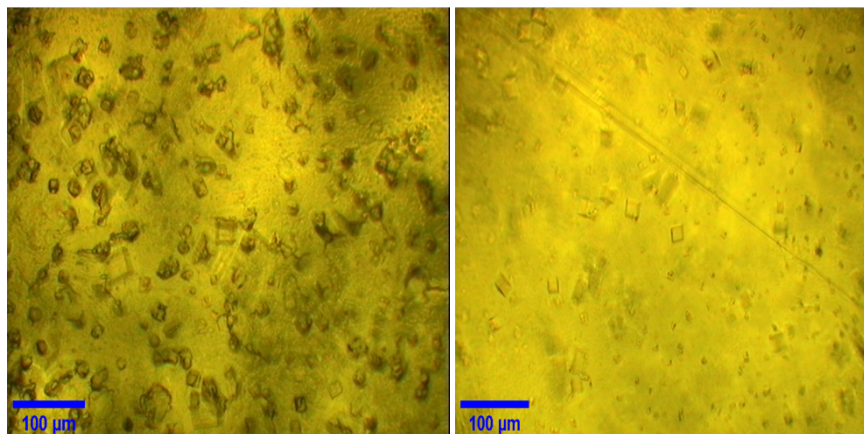


Figure 4.24: Raman spectrum of different types of POSS

#### 4.5 Optical Microscopy

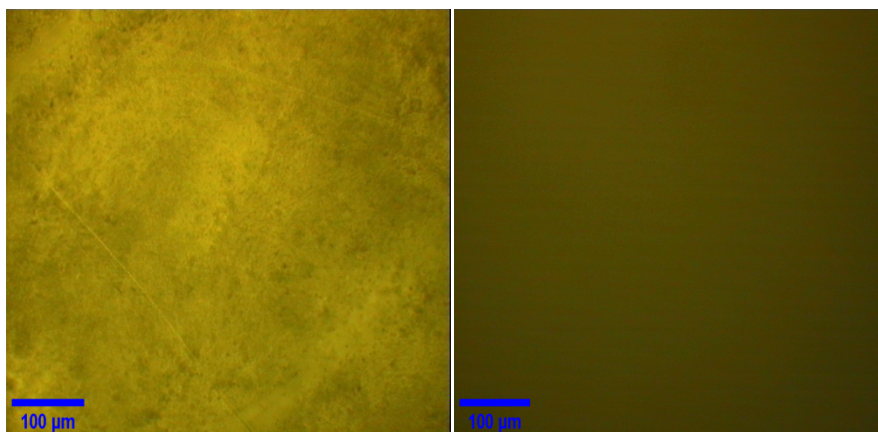
Optical microscopy was used to study the dispersion of the POSS types used in PVP.

Figure 4.24 shows optical images of different POSS-PVP thin films. These images show lack of dispersion in case of MA POSS/PVP and PEG POSS/PVP films.



(a)

(b)



(c)

(d)

Figure 4.25: Optical images of a) 5% MA POSS-PVP b) 5 % PEG POSS-PVP c) 5 % GI POSS-PVP and d) Pure PVP thin films.



## **CHAPTER 5**

### **COST COMPARISON**

Previous works by researchers on incorporating POSS into epoxy matrix for the fabrication of carbon fiber epoxy composites was done through physical blending technique. The amount of POSS used was in weight ratio to the epoxy matrix. Incorporating POSS directly into resin system increases the viscosity of resin system at higher weight percentage POSS loading. This is a great drawback for the vacuum infusion of resins into fiber system.

In this study we incorporated the POSS into the composite system through the use of PVP and the POSS was incorporated only in the interlaminar region. Also the POSS percentage loading was calculated only based on the PVP-POSS solution which makes the amount of POSS used in the system very much less than the direct incorporation of the POSS directly into resin system.

In this study we have developed a cost effective and easy technique of incorporating POSS into composite laminates by reducing the total amount of POSS for a given laminate size and achieving up to 93% improvement in fracture toughness.

A rough cost comparison of cost advantage in terms of POSS percentage was made. In the composite laminates used for this study the resin content is  $36\% \pm 3\%$  volume wise according to the manufacturers. We assume the same weight ratios for rough comparison purposes on a 5% POSS loading. If we are using the direct blending technique the weight ratio of the POSS in the system would be around 2% of the total weight of a given

laminate. If we are using PVP-POSS solution only on the interlaminar region the solution would roughly be 20 % of the total laminate weight (since only one side of each laminate is painted or sprayed with the solution). And, of this 20 % only 5% is weight of the POSS which makes the percentage of POSS in the system of the same size only 1%.

The cost of PVP is negligible compared to the costs of the resin and POSS with POSS having the highest price depending on the type of POSS used. Hence, this reduction by half of the quantity of POSS used will reduce the cost of the POSS modified laminated for any given size with comparable or better results with direct blending of the POSS into the resin system.

Also, a cost comparison between the three POSS types was made based on the materials used to prepare a 0.127 m x 0.230 m DCB samples. Only the percentage POSS loading in PVP that resulted in the maximum  $G_{IC}$  were considered for cost comparison between the three types of POSS. These are 5% GI POSS loading in PVP, 3% MA POSS loading and 3%PEG POSS loading in PVP. Actual costs from manufacturers were used.

Table 5.1 Cost comparison for different POSS/ PVP modifications.

Type of POSS	% POSS in PVP	Cost of PVP (\$)	Costs of POSS (\$)	Cost of Solvents (\$)	Modification cost per unit area (\$/m <sup>2</sup> )
GI POSS	5	0.022	0.08	0.5	20
MA POSS	3	0.022	0.3	0.5	28
PEG POSS	3	0.022	0.02	0.5	18

## CHAPTER 6

### CONCLUSIONS and FUTURE WORK

The interlaminar region of carbon fiber/epoxy laminate was modified using a simple technique of painting or spraying different POSS- PVP solutions. The purpose of the PVP is to act as a carrier material for the uniform distribution of the POSS particles. It is also a good adhesive compatible with most polymer matrices. It was observed that the application of only PVP film in the interlaminar region increased the interlaminar fracture toughness of the carbon fiber epoxy composites by 33%. But, the addition of POSS particles to PVP further improved the fracture toughness up to 93%, which is the case for the Glycidyl Isobutyl POSS. Depending on the type of POSS the percentage of POSS loading in PVP for maximum fracture toughness varied. In case of the Glycidyl Isobutyl POSS maximum fracture toughness was achieved at a 5% POSS loading in PVP. Whereas for the Methacrylate and Polyethylene glycol Isobutyl POSS maximum fracture toughness was obtained at a 3 % POSS loading in PVP.

It was also observed that, even though the maximum fracture toughness was obtained through a POSS with one epoxide group. Satisfactory results were also obtained by the addition of a POSS type with a non-epoxide but highly reactive functional group (MA POSS) and with the incorporation of POSS with no reactive groups (PEG) POSS. The surface morphology of the fractured surfaces also supported this hypothesis.

Regarding the thermo-mechanical properties, DMA results showed that there were no significant changes in the storage modulus of the carbon fiber/epoxy composites with the addition of PVP or PVP/POSS films in the interlaminar regions. It was also observed from the DMA results that the percentage loading of POSS didn't affect the glass transition temperature of the composites considerably and the change in glass transition was mainly due to the addition of PVP. The Raman spectroscopy showed no significant interaction between the PVP and POSS at the POSS loading levels used in this study.

As a continuation of this work, effect of moisture and weathering on the resulting composites should be studied since PVP is highly hygroscopic. Also, inter-diffusion of PVP into epoxy matrix surfaces, changes in the barrier properties, flexural and tensile strength should be studied. The effect of multiple epoxide group POSS should also be studied.

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In this study the interlaminar region of carbon fiber/epoxy laminate was modified using a simple technique of Painting or spraying different POSS- PVP solutions. It was observed that the application of only PVP film in the interlaminar region increased the interlaminar fracture toughness of the carbon fiber epoxy composites by 33%. But, the addition of POSS particles to PVP further improved the fracture toughness up to 93%. It was also observed that, even though the maximum fracture toughness was obtained through a POSS with one epoxide group. Satisfactory results were also obtained by the addition of a POSS type with a non-epoxide but highly reactive functional group (MA POSS) and with the incorporation of POSS with no reactive groups (PEG) POSS. The SEM of the fractured surfaces also supported this hypothesis.

Regarding the thermo-mechanical properties, DMA results showed improvement storage modulus of the carbon fiber/epoxy composites with the addition of PVP/POSS in the interlaminar regions. It was also observed from the DMA results that the percentage loading of POSS didn't affect the glass transition temperature of the composites considerably and the change in glass transition was mainly due to the addition of PVP.

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