FRACTURE BEHAVIOR AND TIME DEPENDENT RECOVERY OF POSS–EPoxy NANOCOMPOSITES

By

KUNAL MISHRA

Bachelor of Technology in Mechanical Engineering
Uttar Pradesh Technical University
Lucknow, UP, India
2008

Master of Science in Mechanical Engineering
Oklahoma State University
Stillwater, OK, USA
2011

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FRACTURE BEHAVIOR AND TIME DEPENDENT RECOVERY OF POSS–EPOXY NANOCOMPOSITES

Thesis Approved:

Dr. Raman P. Singh
Thesis Advisor

Dr. Ali K. Kalkan

Dr. Sandip Harimkar

Dr. Ranji Vaidyanathan
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This study investigates the fundamental mechanism that governs the influence of glycidyl POSS on the time–dependent behavior of epoxy–POSS composite as a function of added weight percent. Different formulation of POSS–epoxy composites were prepared using simple mixing technique. Dynamic mechanical analysis were used to study different transition occur in polymer chain as a function of temperature. The dampening effect of POSS inclusion in epoxy resin was observed by change in Loss Modulus and tan delta. Time temperature superposition principle was applied successfully to the storage modulus and loss modulus. Master curve obtained from TTS indicated the satisfaction of quality. The resulting shift factor was correlated with a significant increase in the free volume in molecular network. Increasing POSS loading showed no sign of phase separation as derived from master curve and thermodynamic gap in CTE. Concerning viscoelastic modeling, Generalized Maxwell model was used to generate viscoelastic parameters for predictive information of nanocomposite. The model showed a good agreement between the theoretical and experimental viscoelastic properties. To further understand the rate–dependency of POSS–epoxy nanocomposite, tensile experiment at different rate were performed. Results showed that with increase in loading rate the modulus of the nanocomposite increases also change in failure mode was observed. XRD on the fractured sample was done to investigate site of deformed energy from the observation of stress–induced crystallinity. XRD spectra also showed that with increase in the loading of the POSS in the composite intensity of crystalline peaks increases. Fracture toughness of the nanocomposite was performed according to ASTM standard at cryogenic temperature. 100% increase in fracture toughness was observed in 5 wt.% POSS loading. Dynamic characterization of the POSS–epoxy nanocomposite takes place using Split Hopkinson Pressure Bar at high strain rates (400–800 s\(^{-1}\)). Single loading pulse of 550 ms is used to load the specimen. For comparison in strain rate, test at quasistatic rate are also performed. The test results shows that both Young’s modulus and yield strength is sensitive to strain rate. Both dynamic and quasistatic experiment shows increase in the toughness with higher concentrations of POSS.
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CHAPTER 1

INTRODUCTION

Epoxy resins are widely used in various engineering applications, such as aerospace industries, automotive industries etc. This is due to their superior properties that includes high glass transition temperature, high modulus, high creep resistance, and good resistance against chemicals [1, 2]. These properties of epoxy resins are due to the high degree of chemical cross-linking introduced by diglycidyl ether of bisphenols.

In recent years, a considerable amount of work has been done in an attempt to modify the properties of the epoxy either by modification in chemical group of polymer or by reinforcing of a second phase in the epoxy resin. Different reinforcement fillers such as rubber particles [7–11, 13], thermoplastics [14], metal particle [15–20], silicate layer [21–30], ceramic particles [31], glass beads [32, 33], carbon nanofibers [34–38], carbon nanotubes (CNT) [39–43], and combination of two fillers [37, 44] have been used previously with some success.

Mechanical properties of filler reinforced resins can be enhanced by a variety of energy dissipative mechanisms. These mechanisms are dependent on different variables including the chemical nature of filler, filler size, and filler loading. In case of toughening with organic fillers like rubber particles and thermoplastics, energy is dissipated due to shear yielding process. Unfortunately, use of such organic fillers reduces the modulus of the resin system. When inorganic particles with high modulus are used as fillers toughening is observed to occur via various mechanisms of energy dissipation without compromising the modulus. Examples of such toughening mechanisms includes crack pinning, crack bridg-
ing, crack path deflection, and micro cracking. However, inorganic particles tend to form agglomerates at low loadings results in deterioration of epoxy resin properties. So in order to obtain a better dispersion of the nano filler in polymer matrix, researchers have tried several techniques which in turn increase the preparation and fabrication time as well as make procedure complicated.

With the addition of these fillers in polymer matrix, there is a change in the curing kinetics, local stoichiometry, curing reaction and, curing temperature, due to modification in molecular network and also local physical interactions near the particle surface [45].

Compared to conventional micron-sized particle recently, nanoparticles has shown an immense interest in research and development as well as academia. Nanofillers with very high surface-to-volume ratios, and ultrafine size exhibit different properties from the bulk. Various studies in the past compared the micron-sized fillers to nano fillers. Nanofillers showed some unique properties, like interfacial area between matrix and filler. They observed due to this high density of particles per volume (typically $10^6$–$10^8$ particles/mm$^3$), promotes better stress transfer from soft matrix to hard nano particles leading to increase in strength and stiffness of the composite. As a result of this only small amounts of fillers are needed to cause significant changes in composite. Also nano sized filler show better dispersion in polymer compared to micron–sized fillers [45,46].

In terms of nanoparticle dimensionality nanocomposites usually classified into, zero-dimensional reinforced with nanoparticle (fullerenes), one-dimensional reinforced with nanofiber/ nanotube (carbon nanotube, carbon nanofiber), two-dimensional reinforced with nano-film, nano-coating nano-layer: graphene, clay), and three dimensional for its interpenetrating ability in the network systems. Among polymer nano-composites, functionalized polyhedral oligomeric silsesquioxane (POSS) molecules are an interesting class of three-
POSS molecules due to its unique hybrid organic–inorganic properties, nanosize, ease incorporation with polymer, its modification according to different requirement attracted researchers in past. Various researches have been done on the characterization of POSS reinforced materials [63–72]. These have included the study of the formation of nanoscale structure, the synthesis of novel POSS and enhancement of physical properties including thermal degradation and glass transition temperature. In our previous work [62] we employed POSS as a nanofiller due to its unique properties to study the fracture properties of POSS reinforced epoxy resin.

1.1 Literature review on POSS

1.1.1 Characterization of POSS

POSS are low density (compared with conventional inorganic nanofillers), unique hybrid materials that comprise of both organic and inorganic atoms as shown in fig. 1.1. POSS molecules which have been commercialized in the last decade, with the intention to combine the most beneficial properties of both organic and inorganic systems. Because of its unique hybrid properties, the ease of processing, and its various applications in different fields, POSS based nanocomposites have received increasing attention.

Silsesquioxanes are all structures with the general formula $RSiO_{1.5}$. It comes in various structures such as ladder, cage and partially cage structures. These compounds contain 8, 10 or 12 silicon atoms attached on the vertices of the cage. POSS compounds contain a rigid framework, with a diameter of 1–3 nm and also thermally and chemically robust. Molecular structure of POSS is given in fig. 1.2.
Figure 1.1: POSS possess unique organic–inorganic properties. Organic substituent provide compatibility and reactivity while inorganic cage provides rigidity and stability in nano composite.

Figure 1.2: Molecular structure of general POSS
The thermal stability of the organic substituents is compositionally dependent and ranges from 300 to 550°C [78–80].

There are four general classifications of POSS-filled polymers and copolymers [81]:

- **Star type**: These are synthesized by the polymerization of a POSS cage containing multifunctional polymerizable groups which will form 3-D networks.

- **Pendant type**: These are POSS molecules with a single reactive functional group and can be polymerized as a monomer.

- **Bead type**: These are POSS core with two reactive functional groups is incorporated in the backbone of a polymer sometime known as techelic system.

- Non-reactive POSS molecules dispersed in a polymer matrix as simple inorganic filler.

POSS reinforced nanocomposites can be modified just by tailoring the organic group (R), attached on the Si atoms of the cage for specific requirements to get optimum results. Even though POSS documented smallest particles of silica possible, they are physically large compare to polymer dimensions.

POSS can be compatible or incompatible with various polymer, shows different interaction with polymer chain, obtaining blending, tethered, main chain or cross-linked composites [82] as shown in fig. 1.3.

POSS can be used in various applications such as in photoresists, magnetic recording media, adhesive and protective coating films, catalysis, precursors to silicates and preparation of copolymers. Polymeric POSS also showed excellent dielectric and optical properties [83].
Among all the various applications, POSS widely used to prepare nanocomposites for better properties for multifunctional materials. POSS can be dispersed in the polymer matrix based on the various interaction such as by weak (van der Waals, pi–pi interaction, dipole–dipole moment) or strong (hydrogen-bonding, covalent bonding) or both.

### 1.1.2 Properties of POSS

- **As a building blocks for self-assembly**

  One of the most important feature of POSS is to form assembly with a various organic groups, enabling several pattern to design nanocomposites with different topology and architecture to meet the materials performance under different condition. Most common patterns of POSS assembly are lamellar and micelle structures. Various researchers have been investigated POSS assembly with some successs. Leu’s group has synthesized and assembled lamellar-shaped POSS-polyimide [80,84,85]. Cui et al. [86] successfully assembled lamellar structures POSS molecules when blended with mono-tether $P_5T – OH$. Knischka et al. [87] observed micellar and vesicular structures in POSS-based amphiphiles.

During the self-assembly process of POSS, the non-covalent interactions, plays vital rule in facilitating the assembly at nanoscale configurations. From thermodynamic
point of view, pattern formation depends on the reduced surface energy between chemically linked, incompatible blocks. However extended annealing are needed to approach thermodynamically favorable structure morphologies. The percentage of inclusion of POSS in the polymer also play a very important factor in determining the final pattern or structure. For example, at low percentage of POSS, POSS-polybutadiene composites form lamellae that are randomly oriented; while at higher percentage, lamellae are configured parallel [88]. The length of the organic chains in POSS is usually selected as per requirement to control the ratio between the mixing system, and hence to obtain the desired pattern. Zhang et. al. [89] have proven, using molecular simulation, that by changing the content of POSS, the pattern can change from lamellae to micelles.

POSS provides better miscibility between different polymer chains. As observed by Mather et. al. [90], attaching POSS to both ends of polymer chains, creating telechelic molecules, greatly increases the compatibility and reduces the interfacial tension between otherwise immiscible system. Similar observation was made by Huang et. al. [91]. While blending PMMA and PS, POSS attached to PMMA enhances the compatibility between the two polymers due to the attraction between POSS and PS [92], by providing better interfacial adhesion and hence improved fracture toughness.

When attached with other nanofillers, POSS also acts as an intervening agent to adjust the spacing between large nano-particles [93], and modifies the physical, chemical, and electronic behavior [94].

• Thermal and mechanical properties of POSS reinforced nanocomposites
Inclusion of POSS also showed increase in the glass transition temperature is observed for various POSS-polymer systems upon incorporation of POSS. For linear polymers like butyl methacrylate [70], polynorbornyl [69] also in network system inclusion of POSS showed increase in glass transition. Amount of POSS inclusion also play important role in glass transition temperature of nanocomposite. As observed by Li et. al. [95] with small amounts of POSS multi-bonded to vinyl ester, the glass transition temperature is not affected, whereas higher amounts of POSS results in the elevation of glass transition temperature. Huang et. al. [91] observed increased $T_g$ along with increased miscibility in POSS-PMMA/phenolic blends.

To study polymer stability thermal decomposition temperature is important factor. Zheng [96] reported increased thermal decomposition with inclusion of POSS. Thermal stability and mechanical properties are largely improved with inclusion of POSS in the parent polyimide [97].

Several other researchers also carried out investigation of mechanical properties of POSS reinforced nanocomposite. Fu et. al. [98] showed increases in the Young’s modulus for ethylene-propylene copolymer with incorporation of POSS. Pyun et. al. [99] showed increase in $T_g$ and Young’s modulus with incorporation of POSS.

- **Change of free volume in molecular network**

Due to the size of POSS and the interaction between POSS and the polymer, POSS-based nanocomposites exhibit a high degree of unoccupied space in polymer network termed as the free volume. This increase in the free volume of the interstitial nanopores introduced, makes the POSS reinforced nanocomposite the ideal candidate for gas/vapor separation membranes [100–102]. Variation in the free volume can be
controlled by modifying the organic group also by altering the interaction between mixing components. The longer polymer chain provides better packing. This may be because the longer flexible chain have more degrees of freedom for the polymer to fold, and thus are less prone to the steric hindrances imposed by the growing covalent network. Other applications for POSS-based nano-composites include the immobilizing of metal cations, drug or catalyst carrier, and also for nanolithography [103]

1.2 Time dependent properties of epoxy resin

One of the distinctive characteristic of epoxy resin is their relative sensitivity to load exposure for extended periods of time or the rate of deformation imposed on them. This behaviors comes under the concept of viscoelastic behavior. These time dependent characteristic extend from instant rate to very slow deformation.

Strain-rate strengthening and relaxation are two factors of the viscous properties of polymers. It can show the effect of strain-hardening under rapid straining under various temperature conditions. In general a broad range of temperature has to be considered as well as various loading rates in order to be able to extract the wanted viscoelastic information from material in question.

Section below discusses about the theory of viscoelasticity and the previous studies related to viscoelastic behavior of polymer and its subsequent composite.

1.2.1 Theory of viscoelasticity

Viscoelasticity is the time-dependence study of materials. The linear viscoelastic material behavior is based mathematically on either on integral or differential formulation. Vis-
coelastic studies can be investigated in terms of uniaxial tension/compression or dynamical. In this work dynamical experiment is adopted.

The term dynamic mechanical properties refers to the behavior of elastomers when subjected to stresses or strains that varies with time. For example, in creep experiments strain increases with time the stress being held constant, whereas in stress relaxation experiments stress decreases with time under constant strain conditions. The governing equation for the linear theory of viscoelasticity are the same as those for the theory of elasticity with the modification that generalized Hooke’s law of elasticity is replaced by a integral information which is sensitive to the material’s history of loading or deformation.

Figure 1.4 below shows the time dependent response of polymer. When subjected to a constant strain, the stress in polymers will relax (i.e. stress will decrease to a steady state value) as shown in figure. In a linear viscoelastic material the relaxation is proportional to the applied strain, as shown in eqn. 1.
\[
\frac{\sigma(t)}{\varepsilon_o} = E(t)
\]  

(1.1)

Under constant stress polymer will shows creep (i.e. strain will continue to increase to a steady state value) as shown in fig. 1.5. If the creep response is proportional to the applied stress, the material is linear, as shown in eqn. 2. The creep compliance is defined by:

\[
\frac{\varepsilon(t)}{\sigma_o} = J(t)
\]  

(1.2)

For sinusodial response, when the polymer subjected to sinusoidally varying stress there will be a phase angle between the stress and strain. This phase angle creates the hysteresis seen in cyclic stress-strain curves. The phase angle can be related to the damping of the material.

Figure 1.5: Creep compliance curve for linear viscoelastic material.
Usually in the viscoelasticity, the elasticity is represented by a spring, while the viscosity is given by a dash pot, that follows the Newtonian law. The simple model of a viscoelastic body can be represented as a combination of spring and dash pot either in parallel or serial arrangement.

Different types of models were used to show viscous behavior analogy.

- **Maxwell Model**: James Maxwell proposed a model in 1867 that exhibits viscoelasticity. It uses spring and dashpot in series as shown in Fig. 1.6 below. It doesn’t match the creep response well. It predicts a linear change in stress versus time for the creep response.

- **Kelvin Model**: Kelvin model uses spring and dashpot in parallel as shown in Fig. 1.7. It doesn’t match relaxation response well also it doesn’t show time dependent relaxation.
• **Generalized Maxwell Model**: The generalized Maxwell model is a multiple parameter model that contains a Maxwell arm in parallel with an elastic arm. It represents the response of real material accurately than Maxwell or Kelvin model because it include many relaxation times. Equation governing generalized Maxwell model is given below.

\[
\sigma(t) = G(t)\varepsilon_0 \tag{1.3}
\]

\[
G(t) = G_\infty + \sum_{i=0}^{n} G_i e^{-\frac{t}{\tau_i}} \tag{1.4}
\]

\[
\tau_i = \frac{\eta_i}{E_i} \tag{1.5}
\]
\[ G_0 = G_\infty + \sum_{i=0}^{n} G_i \]  

1.2.2 Literature review on polymer viscoelastic behavior

Numerous studies have been done to understand the viscoelastic properties of epoxy resin and filler incorporated nanocomposite.

Theocaris [111] reported the both creep and relaxation experiment through stress and strain optical coefficients, he proved that validity of time-temperature superposition principle can be applied to viscoelastic properties of epoxy resin. Yao et. al. [112] validate the linearity in asphalt incorporated epoxy to check material viscoelastic response also frequency temperature superposition was applicable for asphalt/epoxy nanocomposite.

Tcherbi-Narteh A. et. al. [113] showed that viscoelastic properties of partially cured MMT incorporated epoxy showed higher values prior to and during UV radiation degrada-
tion. Grillet [114] studied the viscoelastic properties of DGEBA based resin with different amine based curing agent, he found out the overall properties of cured epoxy is related to structure of curing agent. Wang et. al. found out modulus of epoxy/cyanite copolymer decrease rapidly with increase in content of epoxy.

Wu et. al. [115] suggested that multi-component structure has large influence on the mechanical and viscoelastic behavior of system. Tcharkhtchi et. al. [116] studied the viscoelastic properties of epoxy/amine network using different ratio of amine, they found out there is not much change in viscoelastic properties with change in amine percentage. Montazeri et. al. [106, 110] studied viscoelastic properties of epoxy resin reinforced with non functionalized and functionalized carbon nano tube, addition of CNT exhibited increase in storage modulus. He also verify viscoelastic properties of nanocomposite using Cole–Cole plots. He found out that the free volume of the nanocomposite decreases with inclusion of carbon nanotube. Gojny et al. [107] reported the effect of MWNT-NH$_2$ on the thermo-mechanical properties of the MWNT/epoxy composites. The results indicated an improvement in the storage modulus in rubbery state as well as loss modulus values. Miyagawa and Drzal [108] reported that the storage modulus of the epoxy-based nanocomposites containing fluorinated SWNT increased, but the $T_g$ decreased linearly with an increase in the amounts of CNTs. Abdalla et. al. [109] showed that using carboxylic and fluorinated nanotubes the storage modulus in the glassy state and the rubbery plateau modulus were higher compared to the neat epoxy.

Numerous research have also been done on the viscoelastic effect of POSS inclusion on different type of polymer.

Li et. al. [104] investigated the viscoelastic response of epoxy/POSS nanocomposites, they found out glassy modulus of the nanocomposites decreases. Also found out $\alpha$-relaxation increase and $\beta$-relaxation suppressed with inclusion of POSS. Kopesky et.
al [105] studied the miscibility and viscoelastic properties of POSS–PMMA blends, they showed phase separation at higher POSS content, also time-temperature superposition (TTS) was applied successfully to storage and loss moduli. Uribe et. al [117] studied the viscoelastic behavior of POSS included styryl based polymer. They found out inclusion of POSS highly affected the viscoelastic properties of parent polymer, as they found out at high temperature rubbery plateau developed.

Most of these studies investigates the phenomena of viscoelasticity from change in glassy/rubbery modulus, also they performed TTS to validate viscoelastic behavior of material over a long period of time using master curve. In this work we studied the variation of modulus in \( \alpha \) and \( \beta \) relaxation state to understand the motion of polymer chain as a function of temperature and time. Also we investigated the dampening (energy in term of heat dissipation) of material in terms of loss-modulus and loss factor (\( \tan(\delta) \)). We employed Time-temperature-superposition (TTS) phenomena to study time-temperature dependency of neat resin and POSS reinforced nanocomposite also to calculate change in free volume using William Lendal Ferry (WLF) equation. Viscoelastic behavior of nanocomposite will be validated using generalized Maxwell model to show correlation it with experimental parameters. Qualitative study of time-dependent recovery in nanocomposite is investigated.

1.3 Properties of epoxy resin at very low temperature

The brittle behavior and low resistance against fracture propagation of epoxy resins becomes more severe at very low temperature. At low temperature polymer chain shrinks and generates internal stress in epoxy resin itself. It makes epoxy resin very brittle and unsuitable for low temperature use. With the rapid developments in spacecraft, superconducting cable technologies, large cryogenic projects etc., epoxy resins have been increasingly employed in low temperature engineering application as an adhesive, in coating or as matrix in fiber–matrix composites [47–51]. This demands the improved mechanical properties of epoxy resins at low temperature by making it suitable for these applications. In order to
develop high performance epoxy resins for cryogenic applications extensive investigation had been reported.

Ueki et. al. [52] reported that the control of the chemical and network structures is very important to optimize epoxy systems for cryogenic engineering applications and they found that the network structure should be given priority over the chemical structure in improving the fracture toughness at cryogenic temperature. Nishijima [53,54] used free space phenomena that defined as the unoccupied space within the molecules and free volume defined as the unoccupied space between molecules in three-dimensional epoxy networks to explain the toughening mechanism at cryogenic condition.

Different type of additives have been used previously in epoxy resin, like carbon nanotube [55,56], hyperbranched polymer [57], flexible diamines [58], exfoliated MMT [60], silica nanoparticles [59], organoclay [61], polyurethane etc., to enhance the mechanical properties at low temperature. Some of these fillers showed promising result in the tensile and impact properties but the limited researches have been done on estimating the fracture toughness of filler–epoxy nanocomposites. Although these fillers showed better properties at room temperature but at the lower temperature these fillers deteriorates the fracture toughness value. As these fillers has different coefficient in thermal expansion (CTE) compare to polymer matrix, at low temperature due to this difference in CTE large residual stresses produce that decreases the intermolecular forces in polymer network. Also it has been reported that these fillers cause interference during the shrinkage of polymer chain.

1.4 Effect of dispersion method on POSS–epoxy nanocomposite

Dispersion of the nanofillers in epoxy resin is still major problem in polymer matrix. Simple mixing technique provides only limited dispersion of the fillers in epoxy resin. With
limited dispersion, chances of forming agglomerates gets high. These agglomerates deteriorates the properties of the nanocomposites. Hence it is very important to disperse nanofillers effectively in epoxy resin for better interaction and properties of nanocomposites. Previously researchers worked on different type of mixing method, such as hand mixing, dispenser mixing, mechanical mixing, shear mixing, ultrasonication or combination of either type, to investigate role of dispersion method in final properties of nanocomposites [74–77]. In our previous work we tried only one type of mixing method to disperse POSS in epoxy resin, that is mechanical mixing. Though mechanical mixing showed good dispersion and mechanical properties, it was important to investigate other techniques of dispersion method for optimum mixing of nanofiller.

The objective of this study is to investigate the thermomechanical, viscoelastic, fracture and self-assembly behavior of POSS incorporated epoxy resin.

1.5 Motivation for this study

In our previous study [62], we used POSS as a nanofiller to investigate the fracture behavior of nanocomposites at a room temperature using simple fabrication technique. Unique organic–inorganic hybrid characteristic and the nanosize of the POSS was one of the motivation to use it as a nanofiller in the epoxy resin. Nanocomposite was prepared using simple mechanical mixing as by nature, POSS can easily dispersed without forming agglomerates. POSS reinforced nanocomposite showed promising result by increasing the fracture toughness value by 2 times compared to neat resin as it also supported by SEM image of fractured surface. The work of fracture increased 4 times that of neat resin. FTIR spectra also showed that POSS exhibit good interaction with the epoxy resin. Also it showed that with inclusion of special kind of POSS derivative the failure of the nanocomposite changes from brittle to ductile. From that work we learned that with the inclusion of POSS in the epoxy resin we
can modify the properties according to our specific requirement.

From that study we understood the kind interaction POSS exhibit with the polymer resin and its subsequent effect in the overall properties of nanocomposite. The change in the failure behavior due to inclusion of POSS motivated us to investigate this change in response in detail. This material response is studied in terms of phenomenological viscoelastic models and a fundamental mechanistic understanding of the deformation in material.

**Objective of this study**

The POSS particles have been used as reinforcing nanomaterials in this study and they can be molecularly dispersed within epoxy resin. POSS contain unreactive/reactive organic groups can be mixed with epoxy resin to modify the characteristics of the resultant composites. Therefore, the properties of the nanocomposite can be improved by the addition of a small content of POSS nanofiller [62]. For this reason, POSS derivatives are potential candidates as reinforcing nanoparticles for the fabrication of the nanocomposites.

The main objective of this study is to investigate the fundamental viscoelastic phenomena of POSS–epoxy nanocomposite using both experimental and theoretical study, also to use this study in different application.

In this study, two different type of resin is used namely Diglycydyl ether of bisphenol A and F based resin (DGEBF/DGEBA) mixed with three different type of POSS namely trisilanol phenyl, glycidyl, and methacryl to investigate properties.

The specific objectives of this project were categorized as follows:

- Preparation of POSS–epoxy nanocomposites, containing different loadings of nanoscaled POSS particles.
• Investigate the influence of the presence of POSS nanoparticles on the thermomechanical properties of the samples using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC).

• Study the phenomena of viscoelastic behavior in neat resin and POSS–epoxy nanocomposite using TTS.

• Study the time dependent recovery of POSS reinforced epoxy resin.

• Develop generalized Maxwell model for neat resin and POSS–epoxy nanocomposite and validate the theoretical parameters with experimental result.

• Determination the effect of the POSS nanoparticles on the mechanical properties of the nanocomposite at subzero temperature.

• Investigate self-assembly phenomena of POSS in the epoxy resin, and its effect on mechanical properties of nanocomposite.

• Determination of the surface characteristics of POSS–epoxy nanocomposite by means of scanning electron microscopy (SEM).

• To predict optimum processing parameter and condition for the specific requirement using work in this study.
CHAPTER 2

Materials and Characterization

The objective of the present work is to investigate the time-dependent behavior of POSS–epoxy nanocomposites and self assembly phenomena of POSS molecule in the epoxy resin. Different type of mixing technique have been used to disperse POSS in the epoxy resin.

2.1 Materials and characterization

2.1.1 Materials

In this work two different type of epoxy resins have been used as a based resin, namely, (I) EPON 862® (Hexion speciality chemicals, Columbus, OH), a diglycidyl ether of bisphenol F (DGEBF) based resin cured with curing agent Epikure 3274®, a low viscosity aliphatic amine [130] and (II) SC79 Part A® (Applied poleramics, Benificia, CA) a diglycidyl ether of bisphenol A (DGEBA) based resin cured with curing agent SC79 Part B®, a cycloaliphatic amine [131].

The reason behind selection of this epoxy resins was their superior mechanical properties, easy handling and also these resins are very well studied in literature and ease of fabrication. Figure 2.1 and 2.2 shows the molecular structure of the DGEBF and DGEBA based resins respectively. Table 1 shows the general properties of the epoxy resins used in this work.

Three different functionalities of POSS were used in this work, namely, trisilanol phenyl, methacryl, and glycidyl POSS. These POSS were purchased from Hybrid Plastics (Hatties-
Figure 2.1: Molecular structures of Diglycidyl ether of bishphenol-F

Figure 2.2: Molecular structures of Diglycidyl ether of bishphenol-A

Table 2.1: Properties of epoxy resins used for this work.

<table>
<thead>
<tr>
<th></th>
<th>Epon 862 [130]</th>
<th>SC79–Part A [131]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Hexion co. ltd.</td>
<td>Applied Poleramics</td>
</tr>
<tr>
<td>Curing agent</td>
<td>Epikure 3274</td>
<td>SC79–Part B</td>
</tr>
<tr>
<td>Curing cycle</td>
<td>24 h at 25°C; 6 h at 121°C</td>
<td>5 h at 121°C</td>
</tr>
<tr>
<td>Fracture toughness</td>
<td>1.1 MPam$^{1/2}$</td>
<td>1.2 MPam$^{1/2}$</td>
</tr>
<tr>
<td>Density</td>
<td>1.17 gm/cc</td>
<td>1.16 gm/cc</td>
</tr>
</tbody>
</table>
Figure 2.3: Molecular structure of general POSS used for this work

These specific variants of POSS were selected based on their interaction with epoxy resin. Non-reactive trisilanol phenyl POSS shows compatibility with epoxy resin through hydrogen bonding, dipole-dipole moment, similar chemical structure and $\pi - \pi$ interaction. The methacrylate group in methacryl POSS react with epoxy resin and form covalent bonds. Glycidyl POSS potentially exhibit both compatibility and reactivity with the epoxy resin. As glycidyl POSS showed interesting behavior while incorporating with epoxy, we selected this POSS in most part of study.

2.2 Sample preparation

To study viscoelastic behavior of the nanocomposite only mechanical mixing was used whereas to study self-assembly phenomena of POSS in the resin three different kind of dispersion method was used.

2.2.1 Mechanical mixing

Principle of mechanical mixing

Magnetic stirrer is used as a mode of mechanical mixing for this purpose. Magnetic stirrer basically is driven by the micro-magnet motor produces rotating magnetic field to
drive the rotating stir within the container in order to achieve the fully mixed reaction.

**Mixing POSS and epoxy resin using mechanical mixing**

The liquid epoxy resin was mechanically mixed with POSS overnight at 50°C on magnetic mixture. The mixture was then cooled to room temperature (25°C) under ambient conditions. Heating decreases the viscosity of the resin allowing a more homogenous mixing.

### 2.2.2 Shear mixing

**Principle of shear mixing**

A high shear mixer has a special designed stator/rotor working head. When it works, this stator/rotor head is able to draw the solids and liquids around it into its center, and then push them radially through the stator openings back to the tank. During this experience, the solids and liquids are subject to an action of milling and shearing which is so intensive that they are deagglomerated, homogenized and dispersed into each other even though they are immiscible by traditional agitation. Shear mixing is basically combination of convection where collective transfer of particles takes place from one location to another and diffusion where distribution of particles takes place over freshly developed surface.

**Mixing POSS and epoxy resin using shear mixing**

The POSS was added slowly to the epoxy held at 50°C while mixing at magnetic mixture. After 1 hour of mechanical mixing, resin was placed in an ice bath to maintain optimum temperature and mixed with a shear mixer (T-25 Ultra Turrax, at 15,000 rpm) for 2 hour.
2.2.3 Sonication

Principle of sonication

Particles agitated by applying ultrasound energy and forming acoustic cavitation. The size of acoustic cavitation increases and finally it collapses and change kinetic energy of ultrasound energy into high heat energy. This high heat energy then break and make the intermolecular interaction between particle–particle and particle–resin respectively. When rapid quenching takes place the nanoparticle and epoxy resin accommodate itself in more relaxed state that leads to proper adhesion between polymer and nanoparticle. Figure 2.4 shows formation and explosion of acoustic cavitation with time.

Mixing POSS and epoxy resin using sonication

The POSS was added slowly to the epoxy held at 50°C while mixing at magnetic mixture. After 1 hour of mechanical mixing, resin was placed in an ice bath to maintain optimum temperature and high energy agitation is provided by an ultrasonic disrupter (TM750, Tekmar-Dhormann, Cincinnati, OH, USA) using a 20 kHz frequency and a 5.0 s on-off cycle to break down the agglomerates.

The curing agent was then added to this mixture in the ratio of 100 parts of epoxy resin to 40 parts by wt.% of curing agent. Finally, everything mechanically mixed at room temperature for 10 minutes at 400 rpm. The mixture was then placed in a vacuum chamber for 30 minutes for degassing, in order to remove gas bubbles that were introduced during mixing of epoxy resin and hardener. Finally, the mixture was poured into a pre-prepared mold. For DGEBF based resin it was cured at room temperature for 24 hours and then, the casted resin plate was taken out from mold and put into curing oven for post curing at 121°C (250°F) for 6 hours. For DGEBA based resin curing takes place at 121°C in oven for five hours. The same curing cycle was used for preparing neat resin as a baseline material.
Figure 2.4: Transient cavitation inside the nanoparticle reinforced epoxy resin during sanit-
tation

2.3 Characterization of nanocomposites

2.3.1 Mechanical characterization

Fracture toughness experiment

Fracture toughness of ductile sample was determined by single edge notch bend (SENB) test as per ASTM D–6068 [134]. This test method is to characterize the slow stable crack growth resistance of bend type specimen. Samples were machined from the cast plate as per ASTM standard. A notch was cut using diamond precision saw and crack initiated by tapping razor blade on the tip of notch. The length of notch \( a_o \) was kept between 11.4–12.7 mm according to the ASTM standard. The specimens were loaded under three point bending using universal testing machine. The specimen was loaded to a selected displacement level that is used to produce a crack extension in a desired position. After that specimen was unloaded, and the crack front was marked and break the specimen to expose the fracture surface. The resulting crack fronts were marked \( a_p \) and the crack extension
were measured from fractured surface by looking under microscope. A minimum of seven samples were used to generate complete $J - R$ curve. All specimen must be machined to the same dimensions. The energy required to extend the crack, $U$, was used to calculate $J$. $U$ is determined from the area under the load–displacement curve obtained from test. $J$ is calculated as follows:

$$J = \frac{\eta U}{B(W - a_o)}$$  \hspace{1cm} (2.1)

where: $\eta = 2$

$B$ = specimen thickness

$W$ = specimen width

$a_o$ = original crack length

$J - R$ curve was constructed from $J - \Delta a_p$ as follows:

1. Construct a minimum crack extension line at $\Delta a_p = 0.05$

2. Construct a maximum crack extension line at $\Delta a_p = 0.1(W - a_o)$

3. Divide the interval between the minimum and maximum crack extension lines into four equally paced regions.

4. The data points shall be evenly spaced throughout the interval with at least three data points in first row, two data points in the second quadrant, and at least one data falling in each of the two remaining regions.

Fracture toughness of brittle sample was determined by performing single edge notch bend test as per ASTM D–5045 [135]. Samples were machined from the cast plate with nominal dimensions of $54.0 \times 12.7 \times 6.3$ mm. A 4.5 mm deep notch was cut using a diamond precision saw, and then the tip of the notch was tapped lightly with a fresh razor
blade using a hammer, to initiate a natural pre-crack. The length of notch was kept between 10.2–11.4 mm according to the requirement of the ASTM standard. The pre-cracked single edge notch specimens were loaded under three-point bending using universal testing machine (Instron 5567, Norwood, MA). Tests were performed in a displacement-controlled mode at a fixed crosshead speed of 0.5 mm/min till the point of specimen failure. The load and crosshead displacement were recorded during testing. The fracture toughness of nanocomposites was measured in terms of critical stress intensity factor (K\textsubscript{IC}) calculated from the peak load, as per ASTM D–5045.

The fracture toughness of nanocomposites was measured in term of critical stress intensity factor (K\textsubscript{IC}) calculated by equation 2.

\[
K_{IC} = \frac{P}{B\sqrt{W}}f\left(\frac{a}{W}\right)
\]  

(2.2)

where P is the maximum applied force, B is the thickness of specimen, W is width of the specimen and f is geometry factor given by equation 9.

\[
f\left(\frac{a}{W}\right) = \frac{3S\sqrt{\frac{a}{W}}}{2(1+2\frac{a}{W})(1-\frac{a}{W})^{3/2}} \times [1.99 - \left(\frac{a}{W}\right)(1-\frac{a}{W})(2.15-3.93\frac{a}{W}+2.7(\frac{a}{W})^2)]
\]  

(2.3)

One important step before performing fracture toughness experiment at low temperature was to anneal the samples. When crack was initiated using razor blade, high stress zone was developed near the crack tip and at low temperature crack propagates by itself due to thermal contraction hence gives apparent fracture toughness value. To mitigate this high stress, samples were placed in the oven for 50°C for 1 hour followed by slow cooling in oven itself. Stresses in terms of photoelastic fringes is shown in Figure 2.5 for before and after annealing.
Flexural experiment

Flexural modulus was determined using three point bend method according to ASTM D–790 [136]. Samples were machined from cast plate with nominal dimensions of $110 \times 25.4 \times 6.3\text{mm}$. The flexural modulus was calculated as per ASTM standard.

$$ R = \frac{ZL^2}{6d} \quad (2.4) $$

where $Z = 0.01$, $L$ is span length and $d$ is thickness. Modulus of elasticity is calculated by following equation.

$$ E_b = \frac{PL^3}{4bd^3m} \quad (2.5) $$

Where $m$ is the slope, obtained from the load displacement graph.

The cryogenic condition (77K) was achieved by filling liquid nitrogen in the setup (fig. 2.6) designed in our laboratory. Dry ice bath was prepared by mixing dry ice in ethanol in the set up to achieve temperature of 200K.
Figure 2.6: Testing of sample in lower temperature condition

**Tensile experiment**

Young’s modulus of POSS–epoxy nanocomposite was determined using dog bone shape sample according to ASTM-D3039. Samples were machined from cast plate with nominal dimension of 12.7 mm thickness, 12.7 mm width of narrow section and 57 mm length of narrow section. Gauge length of 25.4 mm was using extensometer was used, to determine changes in the strain accurately. 1 mm/min displacement rate was used to test according to ASTM for rigid sample. Elastic modulus was calculated from stress–strain graph.

**Compression experiment**

**Quasistatic experiment**

Compression modulus of POSS–epoxy nanocomposite was determined using cuboid shape, with nominal dimension of 12.7×12.7×25.4 mm, according to ASTM–D 695. Speed of test was 1.3 mm/min which is standard rate according to ASTM standard. Stress–strain graph was used to determine the compressive modulus of nanocomposite.
High strain rate experiment

Split Hopkinson pressure bar was used to test the nanocomposite in higher strain rate. A conventional SHPB apparatus as shown in fig. 2.7, consist of a gas gun, a striker, an incident bar, a transmission bar, an energy absorption device and data acquisition system.

The specimen was sandwiched between the incident bar and the transmission bar. The impact of the striker launched by compressed gas, on the one end of the incident bar generates elastic waves in incident bar known as incident wave. When the incident wave travels from the incident bar to the specimen, due to the different material between the bar material and the specimen cause mismatch in mechanical impedances, some part of the incident wave is reflected back into the incident bar known as a reflected wave. The rest of the incident wave transmits through the specimen, results compression in the specimen at high rates, then into the transmission bar as a transmitted wave. On the junction of specimen and transmitted bar some of the wave also reflected back to specimen resulting several flow of wave inside the specimen causing failure. [120–122]

The incident and reflected signals are sensed by the strain gages on the incident bar.
whereas the transmitted signals are sensed but the strain gages on the transmission bar. All three signals are recorded with the digital oscilloscope.

During a SHPB experiment, these bars serve as sensors so it must meet some strict requirements for better data interpretation [121]. Such as:

- The pressure bars must remain elastic and the length should be sufficiently long, compare to length of the incident wave to avoid overlapping of the waves.

- Slender bars are recommended to minimize the effects of two dimensional stress wave propagation in the bars.

- The end of the bar in contact with the specimen must remain flat and parallel throughout the test for better transfer of wave and to provide better result.

- Cross-sectional area of the specimen must not to exceed the cross-sectional area of the bars.

One dimensional stress wave analysis on the bars helps to strain rate, strain, and stress histories in the specimen as reported by [119, 121, 122]

\[ \varepsilon_i = \frac{C_0}{L_s} \left[ \varepsilon_i(t) - \varepsilon_r(t) - \varepsilon_t(t) \right] \]  

\[ \varepsilon = \frac{C_0}{L_s} \int_0^t [\varepsilon_i(t) - \varepsilon_r(t) - \varepsilon_t(t)] dt \]  

\[ \sigma = \frac{A_0}{2A_s} E_0 [\varepsilon_i(t) + \varepsilon_r(t) + \varepsilon_t(t)] \]  

where \( \varepsilon_i(t), \varepsilon_r(t), \) and \( \varepsilon_t(t) \) are incident, reflected and transmitted strain histories sensed by strain gages, respectively; \( A_0 \) is the cross-sectional area of the bars ; \( E_0 \) and \( C_0 \) are Young’s modulus and elastic bar wave speed in the bar material, respectively; \( A_s \) and \( L_s \) are
initial cross-sectional area and length of the specimen, respectively. When the specimen is in a state of uniform stress.

\[ \varepsilon_{i(t)} + \varepsilon_{r(t)} = \varepsilon_{t(t)} \]  

Equation (12)–(14) can be simplified as

\[ \varepsilon = -2 \frac{C_0}{L_s} \varepsilon_r(t) \]  

\[ \varepsilon = -2 \frac{C_0}{L_s} \int_0^t \varepsilon_r(t) dt \]  

\[ \sigma = \frac{A_0}{A_s} E_0 \varepsilon \]

Therefore stress–strain data can be derived from the recorded strain gage signals in a SHPB experiment.

**Criteria for dynamic stress equilibrium**

Criterion for stress equilibrium developed considering stresses at both end of specimen:

Parry et. al. [118] defined a "stress equilibrium factor" \( \sigma_{EQ} \) as

\[ \sigma_{eq} = \frac{\sigma_T}{\sigma_I + \sigma_R} \]  

The stress equilibrium is perfectly achieved when \( \sigma_{eq} \) reached unity.

For this study we maintained strain rate from 400-500 s\(^{-1}\). On each pressure bar, two precision 350Ω strain gauges (ED-DY-062AK-350 manufacture by Vishay instrumenten) have been glued on the diametrically opposite sides. To avoid interferences between the record waves the location of the strain gauges must be carefully determined. These two
strain gauges then have been wired to the two arms of a wheatstone bridge circuit as shown in fig. 2.8. Figure 2.8 is a half bridge configuration in which the two strain gauges are connected to opposite arms to amplify the signal of the longitudinal wave. The wave signals from the two Wheatstone bridge circuits are amplified by differential preamplifier (Tektronix ADA400) and then recorded by a digital oscilloscope (Tektronix TDS3014B). From the recorded signal the stress–strain curve can be obtained using equation discussed above.

![Figure 2.8: Half-Wheatstone bridge circuit](image)

### 2.3.2 Fourier transform infrared spectroscopy

Fourier Transform InfraRed (FTIR) is a method of obtaining infrared spectra by first collecting an interferogram using an interferometer of a sample, and then performing a Fourier Transform equation on the interferogram to obtain the full spectrum. FTIR spectrometer collects and digitizes the interferogram using the Fourier transformation algorithm, and displays the complete spectrum. Advantage of using FTIR over conventional dispersive method is that FTIR can measure all of the infrared frequencies simultaneously, rather than
individually, make the scanning process fast.

Fourier transform infrared spectroscopy (FTIR) was performed to investigate chemical interaction between POSS and epoxy. The materials were powdered using simple grinder. Potassium bromide (KBr) was used as a reference powder. POSS–epoxy nanocomposite powder then added to KBr in the ratio of 1 sample to 99 KBr. These powdered samples were loaded in an FTIR spectrometer (Nicolet iS10, Waltham, MA) and subjected to 64 scans at a resolution of 4.0 cm\(^{-1}\). The spectrum was collected at room temperature between 4000 and 500 cm\(^{-1}\).

2.3.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature or time. DSC is used to study phase transitions such as melting, crystallization, glass transitions, curing kinetics and compatibility. The temperature program for a DSC analysis work such a way that the temperature of the sample holder increases linearly and the reference sample has a well-defined heat capacity over the range of temperatures.

Differential scanning calorimetry for thermal analysis of samples was carried out using a Q 2000 DSC (TA instruments, Inc.) under constant flowing nitrogen (flow rate 50 ml min\(^{-1}\)). Approximately 5-10 mg of sample was loaded in an aluminum pan. The instrument was calibrated by employing the temperature and heat of fusion of high purity Indium standard. The thermal histories of all the nanocomposites were the same prior to each experiment.
To study the $T_g$, the samples were first heated to 210 °C at a scan rate of 10 °C /min, held at that temperature for 2 min. to eliminate any previous thermal history, and then cooled to -25 °C at a cooling rate of 10 °C /min. For the second scan, the samples were heated and cooled under the same conditions. The obtained data is extracted from second heating cycle.

2.3.4 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) is a technique that provides the information about the mechanical properties of materials such as the storage modulus, loss modulus and damping factor. In a typical DMA experiment, an oscillating force is applied to a sample as a function of time or temperature and the system analyzes the response of the material to the subjected force. In DMA different measuring setups such as from compression, 3-point bending, shear, tension, single and dual cantilever modes can be performed.

DMA can be used to study the viscoelastic behavior of polymers and their subsequent composites. Since all polymers are viscoelastic in nature, this method is very helpful for evaluating a complex array of phenomena that polymers exhibit in detail.

Polymers can exhibit three thermal transitions, classified as the $\alpha$, $\beta$ and $\gamma$ transitions by their types of motion. When DMA tests are performed from a very low temperature where the molecules are tightly compressed, to higher temperatures, the free volume, $v_f$ starts increasing so that localized bond movements and side chain movements occur. This transition is known as the $\gamma$ transition.

With increasing the temperature, the $v_f$ increases to a point where there is enough space and mobility of the whole side chains and localized groups. This type of transition is called
the $\beta$ transition. When studying a blend system, this is referred to as the $T_g$ of a secondary component in that blend. The $\alpha$ transition is associated with the chain segment mobility in the crystalline phase, probably due to the reorientation of defect areas in crystals.

In this study we performed both isothermal and non-isothermal experiment to investigate the thermomechanical and viscoelastic behavior.

• Dynamic mechanical analysis (DMA) of the POSS–nanocomposites composite samples for DGEBF based resin were analyzed using TA instruments DMA Q800. A Sample of size 60 mm $\times$ 12.7 mm $\times$ 3 mm was prepared and placed in a dual-cantilever clamping mode, with a span length of 35 mm. Three point bending test was carried out simultaneously with heating the sample from 30°C to 200°C at 3°C/min, and by applying a constant sinusoidal displacement of 20 $\mu$m with 1 Hz frequency. Damping coefficient ($\tan \delta$) of the specimen was measured using TA instrument universal analysis software.

• DMA of nanocomposite were also analyzed at different isothermal temperature (-15 to 75°C) at with frequency varies from 1 Hz to 125 Hz to study the viscoelastic properties of nanocomposite. A Sample of size 60 mm $\times$ 12.7 mm $\times$ 3 mm was prepared and placed in a dual-cantilever clamping mode, with a span length of 35 mm.

2.3.5 X-ray diffraction

X-ray diffraction(XRD) is non-destructive technique used to determine structural properties of materials. A diffraction pattern is produced when a material is irradiated with a collimated beam of X-rays. The X-ray patterns generated by this technique provide a structural finger prints of the unknown material.
The X-ray diffraction (XRD) analysis for the crystallinity developed was performed on the samples using $CuK\alpha$ radiation apparatus (Bruker AXS D8-Discover) at 40 kV. The X-ray diffraction (XRD) data were recorded in the range of 2theta angles between 20 and 60 degrees. The identification of the degree of crystallization were determined using the diffraction spectrum.

2.3.6 Electron micrographs

Scanning electron microscopy (SEM) is a technique where a beam of energy focused electron beam is scanned across a sample. In scanning electron microscopy, a thermionic electron source such as a tungsten filament is usually used and is pumped using turbo and ion pumps to maintain the highest possible vacuum. The technique can provide information about the topography, and morphology of the material. If the system is equipped with an energy dispersive spectrometer (EDS), it can also provide information about the chemical composition of the material.

The basic principle of the system is that the electron beam impinges the surface of material, known as primary electron, and generates a splash of electrons, called secondary electrons, with much lower kinetic energies than the primary electrons. An image of the sample surface is constructed by measuring the secondary electron intensity as a function of the primary beam position.

The SEM micrographs were obtained by the (Hitachi S-4800 FESEM, Dallas, TX) field-emission scanning electron microscopy. The surfaces of the samples were coated with gold-platinum up to 50nm by an electro-deposition method by Crissington sputter coater (Redding, CA), to impart better electrical conduction in sample before recording the SEM micrographs. This was done to prevent the accumulation of static electric charge on the sample during electron irradiation.
3.1 Preliminary work

3.1.1 Fracture toughness of POSS–epoxy nanocomposite at room temperature

We investigated the fracture behavior of POSS–epoxy nanocomposite at room temperature. POSS reinforcement showed promising result by increasing the fracture toughness by 200\% [?]. We also observed that with the inclusion of glycidyl POSS the failure behavior of nanocomposite changes from brittle to ductile.

The load-displacement curve of neat resin and 5wt.% POSS–epoxy nanocomposites tested at room temperature are shown in fig. 3.1 for DGBF-F based resin.

From the graph we observed that by inclusion of POSS, maximum load carrying capacity of the nanocomposite increases. Also, other important observation from the graph indicates that by inclusion of glycidyl POSS in epoxy resin the failure mode changes from brittle to ductile. This transition of failure mode from brittle to ductile was observed when addition of glycidyl POSS increased from 1 wt.% as observe from fig. refgpld. Hence linear elastic fracture mechanics (LEFM) is no longer valid for more than 1 wt.% of glycidyl POSS reinforcement.

To calculate true fracture toughness for such kind of materials, elastic plastic fracture mechanics (EPFM) phenomena have been studied and employed. To calculate the tough-
Figure 3.1: Load displacement curve for neat resin and 5 wt.% POSS–epoxy nanocomposites at room temperature

Figure 3.2: Load displacement curve of glycidyl POSS–epoxy nanocomposite at different POSS percentage
ening of ductile nanocomposites, $J - R$ curve [133, 134] have been used. Figure 3.3 shows the variation in the value of $J$ (fracture resistance) with increase in the crack length ($\Delta a_p$).

![Figure 3.3: Variation of $J$ value with the increase in crack extension, for different percentage of glycidyl POSS](image)

$J - R$ (fig. 3.3) curve confirmed that glycidyl POSS–epoxy nanocomposite follows the $J$ integral concept (EPFM phenomena). It has been concluded from $J - R$ curve that inclusion of glycidyl POSS making polymer chain more flexible that leads to ductile behavior in POSS–epoxy nanocomposite. Initially in $J - R$ curve, $J$ increases linearly with crack length because more energy is needed to break the flexible chain. After that $J$ shows no or very less variation with the further crack extension. This may be because required energy to break the same amount of POSS–epoxy chain become constant and leads to steady state crack growth.

We also observed that, from photoelastic fringes (fig 3.4), during that after removal of
the applied load there was a recovery from deformation. This quick recovery indicated the change in viscoelastic behavior with inclusion of POSS.

![Photoelastic fringes](image)

Figure 3.4: Photoelastic fringes represents stress developed (a) when load is applied and (b) after removal of load

Considering this change in failure behavior and recovery from deformation, due to POSS inclusion, we came up with some hypothesis. These assumption is enumerated as follows:

1. Inclusion of POSS in the epoxy resin enhances the viscoelastic behavior in nanocomposite.

2. When removing the applied force, stress inside the sample relaxes and exhibit strong time-dependent recovery phenomena.

3. With the inclusion of POSS, free volume of polymer network increases as shown in fig. 3.5. Free volume is the unoccupied spaces in the polymer network.

4. This increase in the free volume provide the segmental motion in the network. This segmental motion makes the polymer chain flexible hence changes the failure behavior from brittle to ductile.

To prove the above assumption we have performed preliminary thermomechanical experiment.
Figure 3.5: Schematic of illustration of (a) pure epoxy and (b) free volume in POSS modified epoxy chain
3.1.2 Quantitative analysis to estimate free volume

Differential scanning calorimetry

DSC test were performed to explain change in polymer chain motion and to support increase in free volume. The glass transition temperature ($T_g$) for 5 wt.% of POSS–epoxy nanocomposites has been investigated. $T_g$ depends primarily on chain flexibility, crosslinking of composite, intermolecular attraction, and so forth.

Table 3.1: DSC thermogram for DGEBF based resin and 5 wt.% POSS incorporated resin

<table>
<thead>
<tr>
<th></th>
<th>Glass transition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat resin</td>
<td>61.1</td>
</tr>
<tr>
<td>trisilanol phenyl POSS–epoxy POSS</td>
<td>65.9</td>
</tr>
<tr>
<td>methacryl POSS–epoxy POSS</td>
<td>59.2</td>
</tr>
<tr>
<td>glycidyl POSS–epoxy POSS</td>
<td>51.5</td>
</tr>
</tbody>
</table>

Table 2 shows the variation of $T_g$ with the incorporation of POSS. Gycidyl POSS–epoxy and methacryl POSS–epoxy nanocomposite displayed decrease in $T_g$ compared to neat resin. This is because of increase in mobility of the polymer chain by addition of these POSS. Glycidyl and methacryl POSS reacts with the epoxy resin and merge into polymer network, hence increased the free volume in nanocomposites. $T_g$ for trisilanol phenyl POSS–epoxy increased with the incorporation of POSS. This might be due to the restriction of the chain mobility because of steric hindrance due of big phenyl group attached to end trisilanol phenyl POSS.

3.1.3 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) technique was used to measure change in glass transition temperature ($T_g$) and dampening factor ($\tan \delta$) as shown in fig. 3.6. The result showed close agreement with the DSC result obtained in previous discussion.
DMA data also shows decrease in the value of glass transition with the inclusion of glycidyl and methacryl POSS that also supports the increase in size and concentration of free volume.

3.1.4 Study of thermomechanical behavior of POSS–epoxy nanocomposite using DMA

DMA tests are powerful tools for investigation of viscoelastic properties. Furthermore since glycidyl POSS showed greater reduction in glass transition temperature, hence only glycidyl POSS was used to study the viscoelastic behavior of neat resin and POSS–epoxy nanocomposite. The change in storage modulus of neat epoxy resin and reinforced with different content of glycidyl POSS are shown in figure 3.7. The storage modulus determined at 1 Hz frequency was plotted as a function of temperature for epoxy and nanocomposite. Two relaxation transition are observed. A main transition, $\alpha$, in the high temperature re-
Region is associated with the glass transition temperature. Another relaxation, \( \beta \), is below 0°C. The addition of POSS has considerable effect on the glassy state. This is due to the flexible effect of organic part of POSS and also because of interfacial interaction between POSS and epoxy resin. The glassy storage modulus at room temperature increases with the POSS up to some maximum value.

Figure 3.7: Storage modulus for epoxy and nanocomposite with different weight percentage at 1 Hz frequency

Higher the contents of POSS cause a decrease in the modulus. It seems that with the increase in the content of the POSS, the free volume of the molecular network increases resulting in better movement in the chain. The optimum percentage at which modulus is highest is 1 wt.%. The glassy modulus at room temperature is directly related to Young’s modulus. The rubbery modulus was higher for neat resin. After glass transition temperature, molecular chain motion and the amplitude of this motion are very high moreover the flexibility of the chain increases by inclusion of POSS.
Enhanced flexibility of epoxy chain by reinforcing glycidyl POSS provides the objective to study the viscoelastic properties of POSS–epoxy nanocomposite. Figure 3.10 showed the viscoelastic properties of neat resin ranging from $-20^\circ C$ to $55^\circ C$. As expected the storage modulus increases with increasing time and decreases with increasing temperature with glassy behavior observed at lower temperature and higher frequency and rubbery behavior at higher temperature and lower frequency.

There is relatively less attention has been paid to the damping mechanisms of POSS–epoxy nanocomposite. Damping is related to the energy converted into heat and can thus be used as a measurement of viscous component or unrecoverable oscillation energy dissipated per cycle. Loss factor and damping ratio, are essential design parameters for many engineering applications. High damping properties can be achieved in nanocomposites by taking advantage of the interfacial friction between the POSS and the epoxy resin. The damping capacity of the nanocomposites is usually measured by increases in loss modulus at room temperature also increase in tan delta peak. A weak interfacial interaction important role in enhancing the damping properties of POSS–epoxy nanocomposites, although it is detrimental to the mechanical properties of nanocomposites.

The loss modulus (fig. 3.8) at low temperature initially decreased at low POSS loading, which was followed by a increase in value at with increase in loading. The POSS dissipate energy due to resistance against viscoelastic deformation of the surrounding epoxy matrix. At high temperature peak intensity is high for low loading whereas it is low for higher loading.

Tan delta (fig. 3.9) indicates that material has more energy dissipation potential so the greater the Tan delta peak, the more energy material can dissipate. While decreasing Tan delta means that your material acts more elastic now and by applying a load, it has more potential to store the load rather than dissipating it.
It is well known that the $\alpha$ relaxation is associated with conformational crank shafting movements of the main chain, whereas the $\beta$ transitions are associated with movements of the side groups. The assignment of the $\beta$ relaxation to molecular segment motion depends on the chemical structure of the compound.

![Figure 3.8: Loss modulus for epoxy and nanocomposite with different weight percentage at 1 Hz frequency](image)

3.2 Viscoelastic properties of resulting nanocomposite using TTS

To investigate the effect of glycidyl POSS content on the viscoelastic properties, we employed the time–temperature superposition(TTS). TTS is very important method to describe the viscoelastic behavior of the polymers over a broad range of time/frequency. This technique involves the use of temperature-dependent shift factors for the magnitudes of measured time/frequency. If the time–temperature superposition is successful, the use of horizontal shift factors $a_T$, will yield a “master curve” showing viscoelastic behavior over a much larger range of times/frequencies than could be studied at one temperature.
Figure 3.9: Tan delta for epoxy and nanocomposite with different weight percentage at 1 Hz frequency

The empirical principle of time temperature superposition states that the frequency dependences of the complex modulus $G^*(\omega, T)$ at two temperatures are related by a simple scale change.

$$G^*(\omega, T) = G^*(a_T \omega, T_0)$$  \hspace{1cm} (3.1)$$

This principle was found to be valid for both neat resin and POSS reinforced nanocomposite and was utilized to make master curves. $a_T$ are adjustable parameters which are functions of temperature but not frequency. The temperature dependence of the frequency scale shifts was found to obey the empirical William Landal Ferry (WLF) equations. The horizontal shift factor can be calculated as:

$$log a_T = -\frac{C_1(T - T_0)}{C_2 + T - T_0}$$ \hspace{1cm} (3.2)$$

where $T_0$ is reference temperature and $C_1, C_2$ are intrinsic parameters dependent on the reference temperature. The reference temperature for the master curves was selected to be $35^\circ C$ in this study. By fitting the experimental data to the sigmoid models, all the model parameters and the constants of WLF equations can be obtained. This can be done by minimizing the sum of the square errors.

Figure 3.10 showed the storage modulus of epoxy resin and POSS–epoxy nanocomposite at varying temperature in a frequency sweep from 0.05 to 150 Hz.

![Figure 3.10: Storage modulus of neat resin at different isothermral temperature.](image)

In order to build a master curve at reference temperature, temperature factor multiplied by frequency to shift the modulus either right or left. The modulus at high temperature compare to reference temperature shifted left while lower temperature shifted to right. The multiplication factor has to change for every temperature in such away that the measured values achieve final smooth curves. Figure 3.11 showed the master curve generated using (WLF) equation.
Figure 3.11: Storage modulus of 5 wt.% POSS reinforced nanocomposite and Master curve generated using WLF equation

The master curve of epoxy and POSS–epoxy nanocomposites as shown in fig. 3.12 indicate that the glassy modulus first increases and then decreases with increasing POSS content.

This expected behavior can be explained in the terms of free volume and motion of polymer chain. When POSS was added to epoxy in lesser content the silica cage obstructed the motion of chain results in increasing of glassy modulus while at higher content the increase in free volume offset the effect of silica cage hence aide in chain motion thereby decrease in modulus.

The TTS shift factors, $a_T$, obtained from the construction of the masters curve using WLF equation discussed above. The value of the constant $C_1$ and $C_2$ were determined by plotting $\log a_T$ against temperature. The figure 3.13 showed the shift factor as a function of temperature.
Figure 3.12: Master curve generated using WLF equation for neat resin and POSS reinforced nanocomposite

Dots showed experimental value of shift factor while solid lines shows fitting using WLF equation. It is important to note that the WLF–equation has been derived under assumption generally valid near the phase transition. Hence the WLF-shift function should be applied in the temperature range associated within the range of glass transition temperature. The WLF coefficients are reported in Table 1. $C_1$ and $C_2$ are related to $f_g$ (the fractional free volume at the glass transition temperature). Since with the addition of POSS the structure of polymer changes, it means $C_1$ and $C_2$ vary as the network structure changes. The proportionality between $C_1$ and $C_2$ is considerably larger for network structure as reported by [125]. According to the obtained result, the more POSS is added, the more $C_2$ increases, but $C_1$ decreases. The particular values of linear polymers are ($C_1 \approx 17$, $C_2 \approx 53.8$ K). In other words, the closer the network structure is to a linear polymer and composites; the larger is the difference between its WLF constants and pseudo universal ones.

*Free volume characteristic*
From the free volume theory [123, 124]

\[ C_1 = \frac{B}{2.303 f_g}; C_2 = \frac{f_g}{\Delta \alpha} \]  

(3.3)

where \( B \) is a constant generally considered close to unity, \( f_g \) is the free volume fraction at \( T_g \) and \( \alpha \) is the thermal expansion coefficient. It is possible to identify \( \Delta \alpha \) with \( \Delta \alpha = \alpha_r - \alpha_g \), that is difference between CTE above and below \( T_g \).

Dividing \( C_2 \) by \( C_1 \), we can calculate \( f_g \) [123]:

\[ f_g = \left( \frac{\Delta \alpha B C_2}{2.303 C_1} \right)^{1/2} \]  

(3.4)

Table. 3.2 shows the relationship between the percentage of POSS, CTE, and free volume fraction.

As it was expected both \( \Delta \alpha \) and \( f_g \) increases with the inclusion of POSS. The differ-
Table 3.2: Parameters obtained from WLF equation and free volume fraction calculated

<table>
<thead>
<tr>
<th></th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_2/C_1$</th>
<th>$\alpha_g$</th>
<th>$\alpha_r$</th>
<th>$f_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat resin</td>
<td>288</td>
<td>1925</td>
<td>6.68</td>
<td>$67 \times 10^{-6}$</td>
<td>$136 \times 10^{-6}$</td>
<td>0.01383</td>
</tr>
<tr>
<td>1 wt.% Nanocomposite</td>
<td>23.80</td>
<td>1960</td>
<td>8.16</td>
<td>$70 \times 10^{-6}$</td>
<td>$13.83 \times 10^{-6}$</td>
<td>0.0122</td>
</tr>
<tr>
<td>5 wt.% Nanocomposite</td>
<td>227</td>
<td>2105</td>
<td>9.27</td>
<td>$69 \times 10^{-6}$</td>
<td>$13.80 \times 10^{-6}$</td>
<td>0.0097</td>
</tr>
</tbody>
</table>

The potential between the fractional free volume of the unfilled epoxy ($f_g 0.01383$) and the 5% blend ($f_g 0.0097$) is $0.00386$, or $3.86 \times 10^{18} \text{nm}^3/\text{cm}^3$ of the blend. For 5 wt.% there are $1.2 \times 10^{19}$ POSS molecules per $\text{cm}^3$ of the blend (assuming all $T_8$ cages); from these values we may infer that the amount of free volume generated per added POSS molecule is $0.380 \text{nm}^3$. The $T_8$ glycidyl POSS cage has an approximate diameter of 2 nm, which corresponds to a hydrodynamic volume of $3.82 \text{nm}^3$. This increase in the free volume corroborate the ductility of epoxy with increase in POSS content.

### 3.2.1 Modeling of Viscoelastic Behavior of an POSS–epoxy nanocomposite

The shift factor for each testing temperature can be found as long a the master curve for each specific reference temperature is valid. In previous section we used WLF equation to fit the shift factor data and after best fitting we found $C_1$ and $C_2$ value at reference of temperature $35^\circ \text{C}$. The most common model for the viscoelastic polymer is generalized Maxwell model. In this study generalized Maxwell equation was used to as an equation for fitting the experimental curve. The generalized Maxwell equation used to convert DMA data into Prony series data is:

\[
G'(\omega) = G_0 \left[ 1 - \sum_{i=1}^{N} g_i \right] + G_0 \sum_{i=1}^{N} \frac{g_i \tau_i^2 \omega^2}{1 + \tau_i^2 \omega^2} \tag{3.5}
\]

\[
G''(\omega) = G_0 \sum_{i=1}^{N} \frac{g_i \tau_i \omega}{1 + \tau_i^2 \omega^2} \tag{3.6}
\]
Where \( N \) is the no of elements, \( G_0 \) is the instantaneous stress relaxation modulus, \( \tau_i \) is relaxation time, \( g_i \) is coefficient depends on material property. These equation determine the storage and loss modulus for a given Prony series. In this study we are interested to know that if we calculate the \( G'(\omega) \) and \( G''(\omega) \) then what will be of Prony series parameter \((G_0, N, \tau_i, g_i)\). To find this parameter we guessed initial Prony series parameters to calculate \( G'(\omega) \) and \( G''(\omega) \). Then we calculated the residual difference between experimental and calculated dynamic value. We used MATLAB® code to minimized the residual difference using simplex method. Fig. 3.14 shows the fitting of the Prony series parameter value with the experimental value for 1 wt.% POSS reinforced composite with varying number of parameter. It can be seen from the graph that the model shows very well conformity with the experimental value at \( N=6 \).

![Figure 3.14: Curve fitting of Prony series parameter with experimental value at different parameter using simplex method.](image)

Table 3.3 showed the Prony series parameter for epoxy resin and POSS reinforced
nanocomposites.

Table 3.3: Prony series parameters obtained from curve fitting

<table>
<thead>
<tr>
<th></th>
<th>Neat resin</th>
<th>0.5 wt.% NC</th>
<th>1wt.% NC</th>
<th>3wt.% NC</th>
<th>5wt.% NC</th>
<th>8 wt.% NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_0$</td>
<td>3870</td>
<td>393.81</td>
<td>3.8715</td>
<td>3820</td>
<td>333.81</td>
<td>3032</td>
</tr>
<tr>
<td>$g_1$</td>
<td>0.02</td>
<td>0.03</td>
<td>0.018</td>
<td>0.2</td>
<td>0.13</td>
<td>0.63.8</td>
</tr>
<tr>
<td>$\tau_1$</td>
<td>0.002</td>
<td>0.002</td>
<td>0.003</td>
<td>0.001</td>
<td>0.015</td>
<td>0.055</td>
</tr>
<tr>
<td>$g_2$</td>
<td>0.008</td>
<td>0.023</td>
<td>0.037</td>
<td>0.352</td>
<td>0.13.86</td>
<td>0.631</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>0.002</td>
<td>0.002</td>
<td>0.120</td>
<td>0.170</td>
<td>0.001</td>
<td>5.19</td>
</tr>
<tr>
<td>$g_3$</td>
<td>0.357</td>
<td>0.812</td>
<td>0.029</td>
<td>0.076</td>
<td>0.312</td>
<td></td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>0.002</td>
<td>$2.1 \times 10^{-5}$</td>
<td>0.020</td>
<td>0.003</td>
<td>2.210</td>
<td></td>
</tr>
<tr>
<td>$g_{3.8}$</td>
<td>0.73.83</td>
<td>0.111</td>
<td>0.726</td>
<td>0.292</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_{3.8}$</td>
<td>$8.81 \times 10^{-5}$</td>
<td>0.003</td>
<td>$3.31 \times 10^{-5}$</td>
<td>2.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$g_5$</td>
<td>0.036</td>
<td>0.003.8</td>
<td>0.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_5$</td>
<td>0.061</td>
<td>0.003.8</td>
<td>0.318</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$g_6$</td>
<td>0.026</td>
<td>0.811</td>
<td>0.005</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_6$</td>
<td>1.32</td>
<td>20.13.82</td>
<td>0.73.83</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is interesting to observe that with increase in POSS content the best fit achieved in less number of elements. With increase in the POSS content the viscous part start dominating results in achieving accurate model with less number of element. This increase in the viscous part supports the change in failure behavior with increase in POSS content. These parameters can be further used to determine material properties, and analysis in mechanical behavior based on the change in parameter value.

3.2.2 Time dependent recovery of POSS–epoxy nanocomposite

In master’s work [62], while working with glycidyl POSS in addition to change in failure behavior the unbroken sample retained the shape after sometime. As mentioned in previous section that with inclusion of the POSS molecule the viscoelastic behavior of
the nanocomposite changes drastically. To further investigate the time-dependent recovery of POSS–epoxy nanocomposite we performed tensile test. Figure 3.15 shows the typical stress-strain curve of POSS-epoxy nanocomposite obtained from tensile test of different content of glycidyl POSS.

![Typical stress strain curve of epoxy and POS reinforced nanocomposite at different wt.%](image)

**Figure 3.15**: Typical stress strain curve of epoxy and POS reinforced nanocomposite at different wt.%.

It showed that with inclusion of POSS the maximum stress increases first then start decreasing with POSS content. This behavior can be explained in term of rigidity provided by the silica cage while with increase in POSS content the flexibility of the chain increases that offset the rigidity provided by the silica cage hence decrease the strength. The rigidity in the structure provided by silica cage is further evident by change in elastic modulus as shown in fig. 3.16.

Interestingly change in rate also changed the tensile properties of nanocomposites as shown in fig. 3.17.
Figure 3.16: Variation of elastic modulus of epoxy and POSS reinforced nanocomposite at different wt.%. obtained from tension experiment

Figure 3.17: Stress strain curve for 5 wt.% of glycidyl POSS reinforced nanocomposite at different loading rate
The tension experiment for 5 wt.% POSS–epoxy nanocomposite at different crosshead rate (0.25 mm/min, 0.75 mm/min, 1 mm/min, and 5 mm/min). Figure 3.17 the typical stress–strain graph, for 5 mm/min the sample failed in brittle manner while decreasing the loading speed failure mode start changing from brittle to ductile failure. In the lower strain rate failure mode changes into completely ductile as shown in figure. Also we observed that with increase in strain rate the modulus of the POSS–epoxy nanocomposite also increases. Figure 3.18 shows the modulus as a function of strain rate.

![Graph showing elastic modulus as a function of crosshead rate](image)

Figure 3.18: Elastic modulus of 5 wt% of POSS reinforced nanocomposite at different crosshead rate

This increase modulus with the increase in strain rate relates to the rate hardening of the nanocomposite.

X–ray diffraction (XRD) on the failure surface of these samples showed interesting behavior as shown in fig. 3.19. It showed that there is stress induced crystallinity developed while stretching of the specimen during the experiment as shown by development of some peak.
Interestingly XRD peaks of lower strain-rate sample shows higher intensity compare to higher strain rate sample. This may be because at slow strain rate silica cage in POSS molecules get sufficient time to orient in the direction of loading while at high strain rate the crystallization peaks are low which means silica cages are not getting sufficient time to directional stretching.

Figure 3.21 shows that intensity of crystalline peaks increase with the increase in loading wt.%. This change in the intensity peak may be due to the increase in the POSS nanoparticles.

Figure 3.20 showed the decrease in the intensity peaks for 0.25mm/min sample with time, and ultimately completely diminishes. This diminishing of peaks indicate the shape
Figure 3.20: X-ray diffraction of POSS reinforced nanocomposite experimented at 0.25mm/min after some duration

Figure 3.21: X-ray diffraction of POSS reinforced nanocomposite at different wt.%
recovery of stretched silica cage. Bending of silica cage is furthermore shown to be evident in ATR–FTIR on stretched and non-stretched surface of POSS–epoxy nanocomposite. Figure 3.22 showed ATR–FTIR spectroscopy of POSS–epoxy nanocomposites, at wavenumber $900 - 950\, cm^{-1}$ we observed split peak on the stretched surface compared to non-stretched surface.

![Figure 3.22: FTIR spectra of stretched and non-stretched surface of POSS–epoxy nanocomposite obtained by ATR–FTIR](image)

This splitting of peak suggests bending of Si-O-Si bonds at O atom. Which suggest that there is some residual stress in silica cage after loading is removed that diminishes with time. It is also observed that the loading rate govern the peak position while the relaxation time govern the intensity of peak. Figure 3.23 shows the ATR–FTIR spectroscopy of stretched and non-stretched of neat epoxy resin, stretched surface shows little shift of peak around $1120\, cm^{-1}$ toward left, that suggest stretching of epoxides group while loading.
Figure 3.23: FTIR spectra of stretched and non-stretched surface of neat resin obtained by ATR–FTIR.
This change in the peak was attributed to the gradual weakening of existing mutual interactions in atoms and development of new interaction. An alternative theory is that the peak position shift is caused by the change in the population of different chemical species. In this case, the position of peak maximum tends to shift due to the variation in the relative intensity contributions of closely overlapped bands with their individual frequencies essentially unchanged.

This interesting time–dependent recovery of POSS–epoxy nanocomposite after removal of loading, conclude the behavior of POSS as an analogy where organic group can be modeled as spring and dashpot while silica cage as elastic spring.

As discussed above the inclusion of POSS in the epoxy resin modified the molecular network by increasing the free volume and also it exhibit strong time-dependent recovery. In order to understand how these variation in the polymer network with the introduction of POSS effect the mechanical properties, we investigated it using by performing fracture, flexural and high strain rate compression experiment.

3.3 Mechanical properties of POSS–epoxy nanocomposites

3.3.1 Fracture behavior of POSS–epoxy nanocomposites at low temperature

As from Table 3.2 we observed that the free volume of the nanocomposite increases with the percentage of POSS inclusion. This increase in free volume increase the segmental motion in the polymer network. This help in reducing the thermal stress at very low temperature and hence increasing the intermolecular forces. This increase in intermolecular forces and reduction in residual stress motivated us to study fracture behavior of POSS–epoxy nanocomposite at low temperature.
POSS were added as a reinforcement in epoxy resin at 77K. Figure 3.24 shows that epoxy resin and POSS–epoxy nanocomposites fail at the higher load at 77K compared to room temperature. POSS–epoxy nanocomposites also shows brittle failure at 77K. Figure 3.25 shows the fracture toughness of neat resin and POSS–epoxy nanocomposites at 77K.

![Load displacement curve for neat resin and 5 wt.% POSS–epoxy nanocomposites at 77K](image)

Figure 3.24: Load displacement curve for neat resin and 5 wt.% POSS–epoxy nanocomposites at 77K

It has been apparent from figures that the fracture toughness of the neat resin itself increases by 120% by lowering the temperature. It may be because of increase in the intermolecular forces due to free volume at low temperature. Also, similar to the room temperature behavior, the fracture toughness at 77K increases with the incorporation of POSS attaining the maximum value then value of fracture toughness drops which may be due to formation of particles agglomerates. Trisilanol phenyl POSS incorporated composite shows maximum fracture toughness at 3 wt.% but after that it starts decreasing while in case of methacryl and glycidyl POSS incorporated composite it shows maximum fracture toughness at 5 wt.%. Especially among all the three POSS used, glycidyl POSS reinforce-
Figure 3.25: Fracture toughness of neat resin and POSS incorporated nanocomposites of different wt.%, at 77K

...ment shows better result. In case of glycidyl POSS–epoxy composite the fracture toughness increases up to 1.5 times than that of neat resin at 77K.

3.3.2 Flexural behavior of POSS–epoxy nanocomposites at low temperature

There is no variation in the value of flexural modulus have been observed with incorporation of POSS at 77K. This may be because at very low temperature there is shrinkage of polymer chain hence the flexibility of bonds gets restricted. Due to the high thermal stress, intermolecular forces increases hence the flexural modulus of neat resin and POSS–epoxy nanocomposites at 77K is more than that at room temperature as shown in fig. 3.26.
3.3.3 Scanning electron microscopy of fractured surface

Figure 3.27 shows the electron micrograph of the fracture image of neat resin and POSS incorporated nanocomposites.

For neat resin, fractured surface shows smooth characteristic exhibiting typical brittle failure mode. Nonetheless the rough surface appear on the POSS modified nanocomposites indicates the high energy required for the crack propagation. These rough fracture surfaces exhibits tortuous crack, ridges and river marks that explains the toughness provided due to crack deflection, crack pinning, particle bridging phenomena.

3.3.4 High strain rate response of POSS–epoxy nanocomposite

As mentioned in the introduction, the properties of polymer are strain rate dependent. It is also documented in the literature [126–129] that particle reinforced polymer showed
Figure 3.27: SEM images of fractured surface of (a) Neat resin (b) trisilanol phenyl POSS–epoxy (c) methacryl POSS–epoxy and (d) glycidyl POSS–epoxy nanocomposite.
tremendous rate hardening when subjected in split hopkinson bar test. As we proved above the POSS–epoxy nanocomposite is highly strain rate dependent. We investigated high strain rate response of POSS–epoxy nanocomposites using SHPB. Compression test at quasistatic rate is also performed to compare the rate dependency of POSS–epoxy nanocomposite.

Fig. 3.28 shows the pulse acquired during a test of POSS-epoxy nanocomposite, from the incident and transmitter bars. Superposition of pulses shows that equilibrium achieved during experiment which is also evident by the forward and backward stress in the sample.

![Stress vs Time](image1)

**Figure 3.28:** Pulse acquired from the incident and transmitter bars, shows equilibrium achieved during experiment

The measure stress strain curve of POSS–epoxy nanocomposite for high strain and quasistatic rate are shown in fig. 3.29. We observe that the maximum stress of the POSS–epoxy nanocomposite for high strain rate exhibit maximum stress of 225 MPa for neat resin while with inclusion of POSS it show the maximum flow stress decreases and it shows minimum of 180 MPa for 8 wt.%. This decrease in the flow stress due to inclusion
is may be because the flexibility of the organic group on the POSS increases the movement in chain. At high strain rate the silica cage is not able to response and provide rigidity in the structure.

Figure 3.29: Stress–strain graph response of POSS–reinforced nanocomposite at high strain rate

While at quasistatic rate the maximum stress increases with inclusion of POSS attained maximum stress of 90 MPa at 1 wt.% then start decreasing with inclusion of POSS attaining 50 MPa at 8 wt.%.

The increase in the compressive strength is due to the rigidity provided by silica cage as it get time to response under applied load while with increasing POSS content the increase the free volume hence increase the flexibility in the chain motion hence decreasing the compressive strength.

3.3.5 Self assembly of POSS using different dispersion technique

Self assembly has attracted great interest in scientific field as it generates organized structure or pattern on a wide range of scale especially the nanoscale. It can be accomplished by
various interactions such as hydrogen bonds, van der Waals forces, covalent bonds, $\pi - \pi$ interaction, dipole–dipole moment. In order to understand the phenomena of self assembly of POSS at nanoscale in various pattern we adjusted the polymer architecture and also the process parameters such as temperature, dispersion method, and medium. The pattern mainly depends on the volume fraction of POSS, interaction parameter, with existence of novel polymerization technique the polymer can be designed for the desired requirement.

In this study DGEBA based resin was selected as co-block polymer. Since glycidyl POSS was showing better interaction with resin and forming better network compare to other POSS. In this study we selected only glycidyl POSS as a nanofiller.

Figure 3.30: Stress–strain graph response of POSS–reinforced nanocomposite at quasistatic rate

![Stress-strain graph](image-url)
Scanning electron microscopy

Figure 3.31 shows the micrograph of fractured surface of neat resin and nanocomposites tested at 298K, 200K and 77K respectively.

Figure 3.31: SEM images of fractured surface of (a) Neat resin and glycidyl POSS–epoxy nanocomposite prepared by (b) mechanical mixing (c) shear mixing and (d) ultrasonication, tested at room temperature

The hole on the fractured surface of from fig. 3.31 indicated the self assembly aggregated of POSS nanoparticles. The tendency of self assembly into aggregate of POSS in the polymer is high in case of shear mixing and ultrasonication that suggest when nanoparticles possess high energy it becomes more reactive and results in agglomeration. The hole due to pull out of POSS also suggested star-shaped POSS containing polymer. The ridges or the river marks also suggest that some POSS assembled into dendrimers form, this pattern in more prominent in the case of ultrasonication.
Figure 3.32: SEM images of fractured surface of (a) Neat resin and glycidyl POSS–epoxy nanocomposite prepared by (b) mechanical mixing (c) shear mixing and (d) ultrasonication, tested at 200K
Figure 3.33: SEM images of fractured surface of (a) Neat resin and glycidyl POSS–epoxy nanocomposite prepared by (b) mechanical mixing (c) shear mixing and (d) ultrasonication, tested at 77K
Surface morphology at low temperature also indicates the self-assembly aggregation for POSS–epoxy nanocomposites, as shown in fig. 3.32, and 3.33. From the micrographs we conclude that the high energy provided to POSS–epoxy system tend to combine itself and form self-assembly aggregates.

**Mechanical properties**

In order to understand the effect mechanical properties of self-assembly of POSS nanoparticle, we performed various mechanical characterization in three different temperature: 298K, 200K and at 77 K.

![Graph showing fracture toughness of neat resin and glycidyl POSS–epoxy nanocomposite at 298K](image)

**Figure 3.34: Fracture toughness of neat resin and glycidyl POSS–epoxy nanocomposite at 298K**

The critical-stress-intensity factor $K_{IC}$ at 298K, 200K and 77 K of POSS–epoxy nanocomposites is plotted as a function of the POSS content showed in Fig. 3.34, 3.35 and 3.36. $K_{IC}$ was evaluated in terms of Eq. (8) based on the peak load.
Figure 3.35: Fracture toughness of neat resin and glycidyl POSS–epoxy nanocomposite at 77K

Figure 3.36: Fracture toughness of neat resin and glycidyl POSS–epoxy nanocomposite at 200K
The graph includes the average values and the standard deviations corresponding to five tests for the epoxy resin and POSS reinforced nanocomposite. The fracture toughness value increases with the POSS content in all testing temperature. At 298K shear and mechanical mixing attained maximum value at 1 wt.% with an improvement of 20% compared to neat resin. The sample prepared from ultrasonication showed an improvement of 50% increase at 8 wt.%. At lower temperatures similar trend was observed with inclusion of POSS. The fracture toughness value of neat resin increases from $1MPam^{1/2}$ to $1.2MPam^{1/2}$ at 77K and 200K, this may be because at lower temperature the molecular chain shrinks and hence increases the intermolecular forces. The inclusion of POSS increases fracture toughness 30%, 20% and 10% for ultrasonication, shear mixing and mechanical mixing respectively. This increase in the fracture toughness value supported the self-assembly phenomena of POSS molecule in the epoxy resin. The POSS nanoparticle arranges itself inside the matrix in most stable state leading to the better cross-linking in the polymer hence increase the fracture toughness. Increase in the free volume due to inclusion of POSS also played important role in improving fracture toughness at low temperature by reducing the thermal stress in the molecular chain.

**Fourier transform infrared spectroscopy**

To understand the interaction of POSS with epoxy resin, IR spectra of neat resin and 5 wt.% of POSS–epoxy nanocomposite is investigated. From the complete IR spectroscopy not much change was observed while concentrating from wave number 600-1300 cm$^{-1}$, fig. 3.41 we observed the change in spectra with inclusion of POSS. Si-O-Si stretching is observed from wave number 123.87 cm$^{-1}$ and 1120 cm$^{-1}$ and Si-O bending from 820 cm$^{-1}$. The vibration of Si-O bond indicates the proper dispersion of POSS in the epoxy resin. The high intensity of Si-O bending peak is observed in nanocomposites indicates the tendency of POSS to assemble in more relaxed pattern.
Differential scanning calorimetry

The DSC technique was employed to investigate effect self assembly of POSS on the thermal properties of nanocomposites. The glass transition temperature of neat resin showed 187°C. Increase in $T_g$ was observed in the case of nanocomposite prepared from ultrasonication that indicates introduction of POSS content strict the movement of polymer chain by rigid silica cage, which may be due to self assembly of POSS molecule inside the polymer. While in case of the nanocomposite prepared by shear mixing shows almost no change in the value of $T_g$ which may be because the increase of free volume in polymer get overwhelmed by the self assembly of POSS. While in case of the nanocomposite prepared by mechanical mixing the glass transition temperature decreases with POSS inclusion that suggest the increase in free volume offset the self-assembly effect of POSS hence aid in polymer chain movement.
Table 3.4: DSC thermogram for DGEBA based resin and 5 wt.% glycidyl POSS incorporated resin for different dispersion method.

<table>
<thead>
<tr>
<th>POSS–epoxy nanocomposite</th>
<th>Glass transition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat resin</td>
<td>187.1</td>
</tr>
<tr>
<td>Mechanical mixing</td>
<td>175.2</td>
</tr>
<tr>
<td>Shear mixing</td>
<td>185.8</td>
</tr>
<tr>
<td>Ultrasonication</td>
<td>196.5</td>
</tr>
</tbody>
</table>

Different processing parameters leads to variation in the glass transition temperature that might indicates the change in pattern or architecture of nanocomposite. This variation in the pattern formation of the POSS effects the overall performance of the materials.

Figure 3.38: FTIR spectra of 5 wt.% POSS incorporated nanocomposite prepared by mechanical mixing
Figure 3.39: FTIR spectra of 5 wt.% POSS incorporated nanocomposite prepared by shear mixing.
Figure 3.40: FTIR spectra of 5 wt.% POSS incorporated nanocomposite prepared by ultrasonication.

Figure 3.41: FTIR spectra of 5 wt.% POSS incorporated nanocomposite prepared using different dispersion technique from wavenumber 600\,cm$^{-1}$ to 1300\,cm$^{-1}$. 

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CHAPTER 4

SUMMARY

Synthesis and characterization of POSS–epoxy nanocomposites, prepared by dispersion, technique have been successfully carried out at different temperature. Based on the preliminary experiment the following has been concluded

1. Incorporation of POSS in the epoxy resin shows the change in viscoelastic properties of the nanocomposite which was further evident by the Prony series parameter obtained.

2. Using WLF equation the free volume of the nanocomposite was calculated and it showed that inclusion of POSS increases the free volume in the nanocomposite.

3. POSS inclusion also attributed to the time-dependent recovery of nanocomposite after deformation. XRD and FTIR showed some deformation in the cage structure. It also showed that strain rate dependency governs the position of peak while relaxation time governs the intensity of the peak.

4. POSS acts as a positive reinforcement in the epoxy resin for different temperature application. Increase in the free-volume assisted the increase in the fracture toughness value at the sub-zero temperature. Based on the interaction of POSS with epoxy resin enhancement in the value of fracture toughness shows maximum for glycidyl POSS i.e 1.5 times that of neat resin while minimum for trisilanol phenyl POSS i.e 1.1 times that of neat resin, in case of DGEBF based resin. For DGEBA based resin only glycidyl POSS have been used and inclusion of POSS showed increase in the value of fracture toughness at different temperature.
There is no change in the value of flexural modulus have been observed at low temperature considering the scattering in data for all variation of POSS incorporated resin. At room temperature POSS either increased or decrease the flexural modulus depending on the dispersion techniques.

5. Three different type of processing parameters have been used to disperse POSS in epoxy resin to study the self assembly phenomena. SEM images at 20 micron of the fractured surfaces shows the self-aggregation of POSS molecules. This self-aggregation leads to better mechanical properties of nanocomposite. This self-aggregation is more prominent in case where we give high energy while mixing POSS. Hence Ultrasonication showed better self aggregation hence better fracture toughness compare to other processing parameters. For further investigation on pattern TEM and NMR has to be done on the POSS–epoxy nanocomposite.

6. FTIR shows the change in chemical interaction of POSS with epoxy resin with different dispersion method. It also shows POSS is completely consumed by epoxy resin.

7. DSC and DMA shows that with the inclusion of POSS the glass transition temperature changes. This change in the glass transition temperature explain increase in the free volume qualitatively. DSC thermogram also shows change in the glass transition value depends on the different processing parameters.

8. Micrographs of fractured surface of POSS incorporated nanocomposite shows more characters like ridges, hole, shear yielding, river marks compared to neat resin. This surface roughness of POSS incorporated resin explain increase in energy required to crack propagation hence increase in the fracture toughness value.
CHAPTER 5

FUTURE WORK

Use of a POSS in epoxy resin showed promising result at low and room temperature. Phenomena in modifying viscoelastic behavior, time-dependent recovery and self assembly of POSS open the various area to investigate other properties of nanocomposite for specific requirement. Other future work of this research is discussed below.

1. More investigation to analyze high strain properties of POSS–epoxy nanocomposite, using DIC phenomena to investigate strain development compressing specimen.

2. Study quantitative time-dependent recovery of nanocomposite using theory of photoelasticity and DIC on modified SENB sample.

3. Abaqus simulation of fracture toughness experiment using Prony series parameter obtained from modeling.

4. Dynamic fracture toughness of nanocomposite using strain measurement.

5. Investigate self-assembly phenomena of POSS in detail using TEM, NMR etc.
BIBLIOGRAPHY


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VITA

Kunal Mishra

Candidate for the Degree of

Doctor of Philosophy


Major Field: Mechanical Engineering

Biographical:

Personal Data: Born in Gurgaon, Haryana, India on May 15th 1985.

Education:
- Received the B.Tech. degree from Uttar pradesh technical university, Lucknow, Uttar Pradesh, India, 2008, in Mechanical Engineering
- Received Master of Science degree with a major in Mechanical Engineering Oklahoma State University in May, 2011.
- Completed the requirements for the degree of doctor of philosophy with a major in Mechanical and Aerospace Engineering Oklahoma State University in July, 2015.

Experience:
- Worked as a Graduate Research Assistant at the Mechanics of Advanced Materials Laboratory headed by Dr. Raman P. Singh in the area of reinforced nanocomposites