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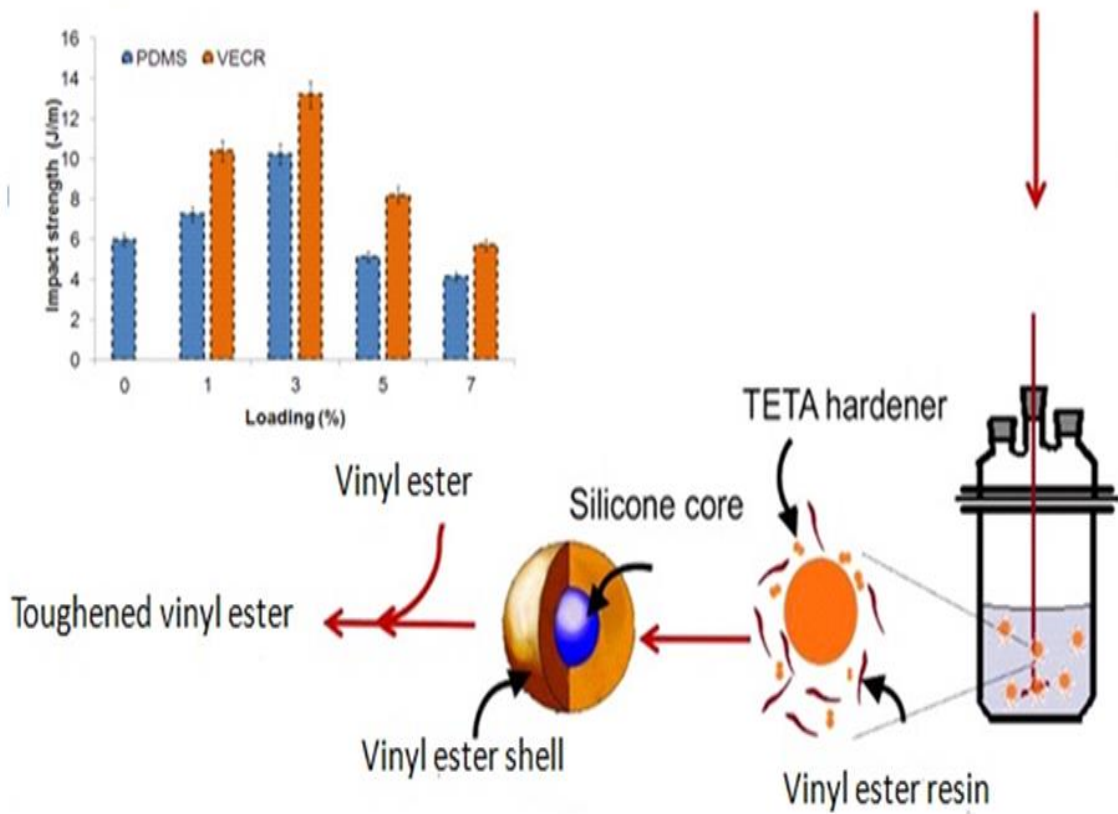
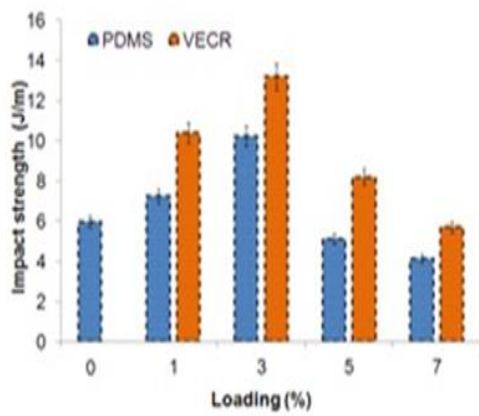
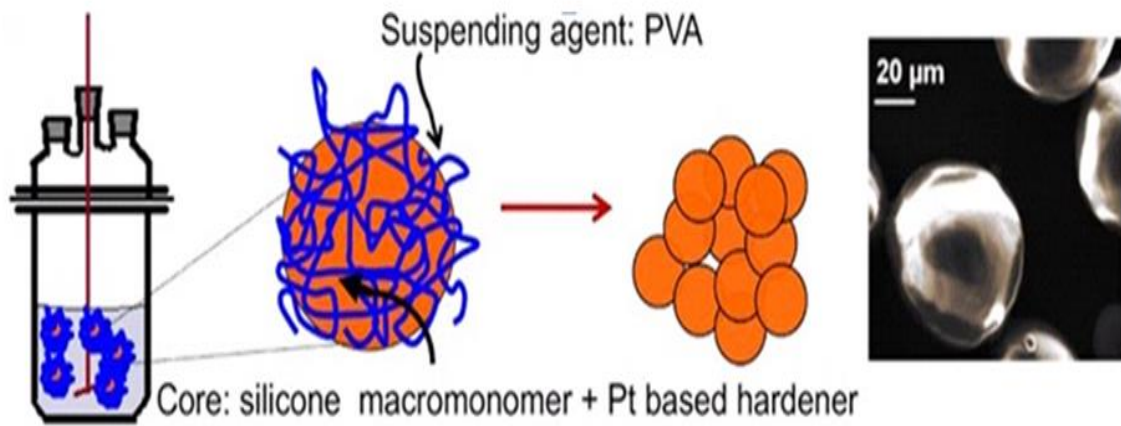
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## ABSTRACT

We report a two-step method for preparation of core shell elastomeric microspheres (CSR) using suspension polymerisation process and demonstrate its potential which proves it as an effective impact modifier for thermosetting vinyl ester resin. The first step involves suspension addition curing of siloxane macromonomer with platinum based hydrosilylation catalyst. The result of reaction parameters on the particle size distribution was decided and the elastomeric microspheres were eventually coated to prepare core-shell (PDMS-vinyl ester) microspheres. Vinyl ester composites were prepared by varying the amounts of microspheres (1-7 % w/w) and consequences of coating on the mechanical properties, that is quasi-static as well as dynamic properties were evaluated. The mechanical properties were found to improve at low loadings ( $\leq 3$  % w/w), and the presence of a vinyl ester coating on the PDMS in the CSR led to improved dispersion, which was evident from its improved mechanical properties. The izod impact strength increased by 132 % on introduction of core shell PDMS – vinyl ester (3% w/w). Morphological studies revealed that the roughness of the fractured surface increased due to introduction of microspheres. In contrast to the PDMS containing composites, where the microspheres were removed entirely due to impact loading, the fractured surface of CSR containing composites revealed the presence of broken microspheres, which is a direct evidence of improved adhesion between elastomeric phase and the vinyl ester matrix. A representative schematic of the entire process is shown in the figure below.



# CHAPTER 1

## INTRODUCTION AND LITERATURE SURVEY

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### 1. Introduction

The emergence of polymeric materials has brought a dynamic change in the face of science and engineering. With the advent of these advanced polymeric materials, light weight and compact structures can be prepared without compromising on the stringent requirements which are required to be met by many engineering products. Several researches have been and are currently underway for the effective utilization of these polymeric materials in various applications. One such application is the area of blast resistance, where tough polymers with high energy absorption characteristic are desirable. The aim of this project is to develop core shell microspheres for the toughening of vinyl ester matrix for their use in applications which resistance to dynamic loads is desired, especially with respect to blast/shock/impact loadings. These polymers can be added as a retrofit layer on existing structures. The primary function of this layer is to hold back the fragments formed as a result of an explosion in place, so that the injury to the inhabitants of the building can be avoided. The polymers that are generally employed for the purpose of retrofitting include polyurea, polyurethanes and vinyl ester.

The following subsections bring out the efforts, which have been directed towards improving the toughenability of thermosetting resins, particularly vinyl ester. The most common route is blending with suitable materials, which improves properties of base resin at relatively low costs compared to synthesizing new polymers. <sup>[1]</sup> The details of the processes commonly employed for toughening of vinyl ester is mentioned under section 1.3. In this context, the oldest method to improve the fracture properties of thermoset resin includes blending of the resin with liquid reactive rubbers. <sup>[2]</sup>

Curing of the thermoset in the presence of rubber leads to its precipitation, and phase separation blends are formed. However, blends with liquid rubber suffer from specific disadvantages including reduced elastic modulus, low glass transition temperatures and high water absorption.

These difficulties can be overcome by using thermoplastics as toughening agents, which has become more common in the last few years.<sup>[3,4]</sup> However, most of the heat resistant thermoplastic modifiers are rather difficult to process. The fracture energy of toughened thermosets is generally proportional to its volume fraction, with the upper limit being of the order of 0.2-0.3.<sup>[5]</sup> Further increase in loading leads to phase inversion, which in turn reflects in terms of reduced mechanical properties.<sup>[6]</sup>

However regardless of the type of polymer used for vinyl ester toughening, it is the thermodynamically and kinetically controlled process of phase separation, which govern the properties of the resultant blend. It is difficult to control this process in fast curing compositions, where phase separation process is hindered leading to minimal improvement in the properties. In view of above, developing ways and means of controlling the morphology has attracted the attention of researchers worldwide. [7,8]

An alternative route towards achieving increased toughness of vinyl ester is inclusion of small quantities of preformed rubbers within the matrix. [2, 9, 10] In this case, the process of phase separation is no longer dependent of thermodynamic and kinetic factors during the curing process, which permits proper control over resultant morphology, thereby leading to larger improvements at much lower loadings.<sup>[11]</sup>

However, due to the incompatible nature of these preformed rubbers and matrix, proper dispersion becomes problematic, which can be solved by coating these with a compatible layer (core-shell polymers).

The larger part of the admissible literature is, however, restricted to core-shell particles in which the elastomeric core is procured from organic rubbers, which are not heat resistant, thereby limiting its use to less demanding application.<sup>[12, 13]</sup> In this context, the use of a thermally stable elastomeric core, e.g. silicone offers a potential solution.<sup>[14-16]</sup>

One of the prime parameters which affect the toughening ability is the particle dimensions of the elastomeric filler. The result of particle size on the fracture properties of vinyl ester has been broadly investigated, according to which it can be said that particles should be quite big to admit their



deformation energy to be higher than their interfacial bonding to vinyl ester matrix, in addition cavitation will not take place.<sup>[11,17][18]</sup> It has been reported that 100-200  $\mu\text{m}$  diameter rubbers are the most efficient impact modifiers, which have reportedly led to over a tenfold improvement in the mechanical properties<sup>[2]</sup>. At present, elastomeric microspheres with an aim of vinyl ester toughening are synthesised by emulsion polymerisation process, but in open literature very few papers describe the synthesis of such materials.<sup>[13, 19, 20]</sup>

We assume that suspension polymerisation process can be used to obtain the elastomeric particles of these dimensions, and the microsphere dimensions can be easily controlled by changing parameters like concentration of the feed solution and stirring speed. The objective of this work was to improve the properties of vinyl ester resins by blending with preformed siloxane elastomeric microspheres. Our motive is mainly to synthesise core-shell poly (dimethyl siloxane) (PDMS) microspheres by a easy suspension polymerization process and then coating with a layer of vinyl ester, which would cause to its apt dispersion within the thermoset.

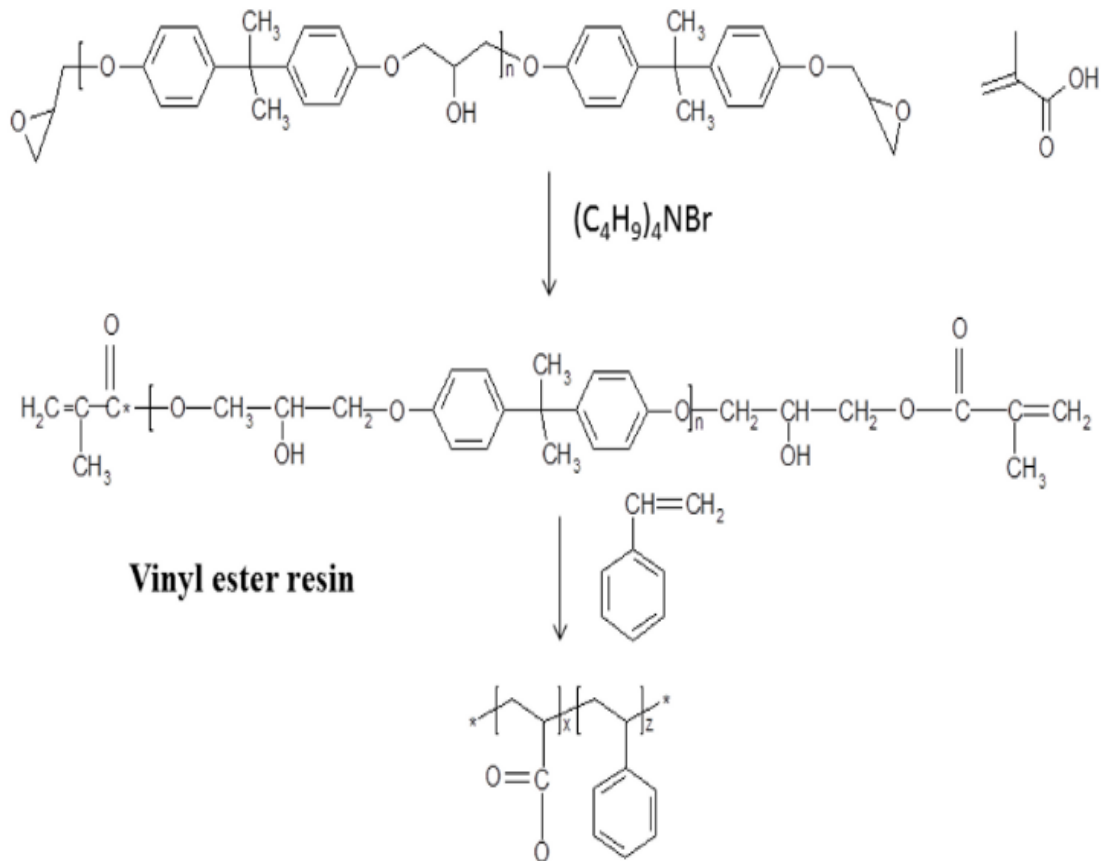
The base polymer which was chosen for the present project is vinyl ester as it has been shown to possess higher tensile strength as compared to polyurea and polyurethanes. The details of vinyl ester system have been discussed in the following sections.

### **1.1. Thermosetting vinyl ester resins**

Vinylester resins are similar in the molecular structure with polyesters, but the location of its reactive sites are available only at the ends of the molecular chains which is quite different from polyester. Throughout the length of the molecular chain of vinyl ester resins shock loading is absorbed which makes it tougher and more flexible as compared to polyesters. Few ester groups are also allocated in the vinyl ester molecule. These ester groups are susceptible to water degradation by hydrolysis which means that vinylesters exhibit better resistance to water and many other chemicals than their polyester counterparts, and are frequently found in applications such as pipelines and chemical storage tanks.

**Vinyl Ester**, or **Vinylester**, which is a resin is produced by the method in which esterification of an epoxy resin is carried out with an unsaturated monocarboxylic acid. After reaction the product which is obtained is then dissolved in a styrene which is reactive in nature, to 35-45 percent content by weight.

The figure shown below depict the idealised chemical structure of a typical vinylester



Scheme 1: Curing of vinyl ester resin

Vinyl ester resins combine the best properties of unsaturated polyesters and epoxies. At room temperature they can be simply managed and have mechanical properties equivalent to epoxy resins. Chemical resistance is superior to low cost polyester resins, mainly hydrolytic stability, and also provide great command over cure rate and reaction conditions than epoxy resins. The unsaturated bonds located on the termini of the vinyl ester oligomers get copolymerized with the comonomer and form a crosslinked network which resembles the curing reactions of unsaturated polyesters. Vinyl

ester resins resembles unsaturated polyester resins as both contain styrene monomer which acts as reactive diluent and also cross link sites are provided by both unsaturated polyester and vinyl esters .

Moreover, the physical properties of the vinyl ester networks are, more advanced to the unsaturated polyesters, mainly corrosion resistance. This implies that vinyl esters have reactive double bonds at the chains end, while in unsaturated polyester resins the reactive double bonds are distributed on the whole length of the chains. So, in the vinyl esters cross link density can be easily controlled. In vinyl ester the chemical resistance is contributed by terminal location of the ester group in the products. It seems that ester groups are liable to degradation by hydrolysis. . In view of the lesser number of such hydrolysable ester groups available with vinyl ester resin in comparison to UPRs, the former exhibits higher chemical resistance and hydrolytic stability. As a result, vinyl ester resin finds immense applications such as pipelines and chemical storage tanks.

## **1.2. Improving energy absorption characteristics of polymers**

The most important criterion for the selection of material to be used for mitigation of blast effects is its capability of absorbing large amounts of energy. Extensile spongy materials which can undergo energy-absorbing molecular rearrangements at the time of deformation are tough , but the tensile strength is lesser. Conversely, rigid hard materials are stiff but they are mainly very brittle having less ability to absorb energy, which results in low toughness.

The property of a material to be able to absorb a large amount of energy during mechanical deformation, without surrendering its stiffness leads to stiffness and toughness of a material. Toughness can be defined as the amount of energy per unit volume that a material can absorb before rupturing. In other words, if the polymer undergoes a transition from brittle to a ductile failure on the addition of a secondary phase, then the material is said to have been toughened. Any material which imparts toughness to an vinyl ester resin is referred to as an “impact modifier”. Toughness can be also stated as the area under the stress-strain curve. Unmodified cured vinyl ester is inherently brittle and has low shrinkage and high creep resistance, which limit their applications in areas which desire high impact fracture strength, or alike thermal cycle resistance.

### 1.3. Thermoset toughening

There are three ways of increasing the toughness of thermoset resins.

- *Addition of rubber particles*

In the first instance, the toughening of polymers by addition of rubber particles appears to be the most adequate route, but a considerable drawback is the reduction in the tensile strength of the specimen. The rubbery phase is miscible with the thermoset resin and the curing agents initially, but as cross linking process starts, the rubber particles tend to form a separate layer. Thus, the initially homogeneous solution separates into two distinct phases and this two phase microstructure leads to increased toughness of thermoset resins.

**Merz et al.** – The rubber particles links the opening fracture surfaces at the cracktip and the fracture phenomenon requires the tearing of rubber particles in which substantial level of energy is absorbed thereby showing increased toughness.

A model for the toughening of thermosets named tear energy toughening has been also proposed.[17] Accordance to this model, the particles stretch over the crack opening subsequently the crack tip and terminate the proceeding of crack.As stated by this model, for a toughened thermoset, the absorbed energy in fracture combines the sum of energy required to break the rubber particles and energy required to fracture a material .[17, 21]

Lately, it has been suggested [22, 23] that the major toughening mechanism is the plastic deformation of the matrix.Plastic deformation tip leads to blunting of crack results in reduction of the local stress concentration and the material can now bear more loads before failure takes place. Excluding the above statements, cavitation of the rubber particles and shear bending of the matrix are also the prime contributors in increasing energy absorption characteristics of rubber filled thermosets.

When a sample is loaded, the rubber particles experience strong triaxial stresses and thus have a tendency to form a cavity. Stabilization of cavity can be achieved by good adhesion, usually because of chemical covalent bonding between the matrix resin and the rubbery domains ; the cavities thus absorb the stresses on the matrix and increase the toughness of the thermosetting polymer. As a result of stress concentration in the matrix caused by the presence of rubbery particles plastic deformation

bands are formed. The plastic deformation in modified thermosets is greater than in unmodified thermosets. When a uniaxial stress is applied on the matrix, a triaxial stress acts on the particles, thus plastic deformation occurs and they become localized and leads to the formation of shear bands that initiates at one particle and terminates at the other.

- *Addition of thermoplastics*

Toughening by addition of thermoplastic domains is another way of improving the toughness of thermosets. Toughing of many thermoset have been done by this way. [24,25].

In 1980's, "rigid-rigid polymer alloy concept" was introduced, when substantial toughening was observed in vinyl ester resins by the addition of a thermoplastic phase. The advantage of using a rigid thermoplastic phase over a soft rubbery phase is that the modulus remains unchanged and so is the tensile strength. Thermoplastics are used either as granulated particles or as polymers dissolved in the liquid vinyl ester which later precipitate out as second phase particles. Polyether sulfone (PES)[29], polysulfone[26], polyether imide (PEI), polyphenylene ether (PPE), polybutyleneterephthalate (PBT) are some of the thermoplastics that have been used as toughening agents for a variety of thermosetting resins.

- *Addition of fillers*

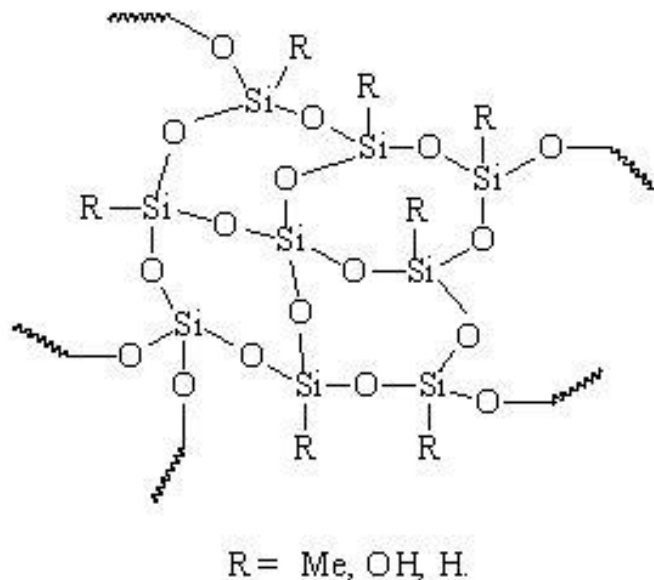
Introduction of filler particles into the polymer matrix is yet another way of improving the toughness of polymers and in this context both hard and soft fillers have been used to improve the toughness. Vinyl ester polymers have also been toughened by the addition these fillers[27] and it has also been suggested that the extent of improvement can be varied by altering the shape and size of the fillers introduced. The increase in toughness is explained on the basis of crack pinning mechanism as proposed by Lange et al[28] and later proposed by Evan et.al. [29]. As stated by this model, the toughness improvement depends on the particle size of filler and the volume fractions. Due to the addition of a brittle and second phase the increased fracture energy of a brittle material was explained by interaction between the propagating crack and the filler phase. Propagation of a crack through the resin, leads to front bowing of the crack between the filler particles but remains pinned at the particles. As a result the growth of the crack is arrested by the addition of fillers. Nanofillers have also been effective in enhancing the impact strength of the fillers reinforced composites [22, 30-32]. In the present study, silicone microspheres have been employed to improve the toughening of vinyl ester.

Because of the incompatible nature of silicone resin and organic matrix, most compositions necessitate introduction of a compatibiliser. Another alternative is the introduction of an additional layer of vinyl ester, i.e. development of core shell PDMS-Vinyl ester microspheres.

The following section deals with silicone rubbers, with a particular emphasis on methods of its preparation and properties.

#### 1.4. Silicone resin

Silicone resins are structurally cage-like having general formula of  $R_nSiX_mO_y$ , where R generally represents Methyl or Phenyl, and X is a functional group H, OH, Cl or OR. Further these groups are densified to have its application in many ways, to give highly crosslinked, insoluble polysiloxane networks.



**Figure 1.1:** Cage like structure of silicone resin

When R is a methyl group, there is a possibility of four types of functional siloxane monomeric units:

- "M" represents  $Me_3SiO$ ,
- "D" represents  $Me_2SiO_2$ ,
- "T" represents  $MeSiO_3$  and
- "Q" represents  $SiO_4$ .

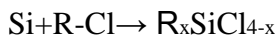
The most found silicone resins are made of D and T units (DT resins) or from M and Q units (MQ resins), Moreover many other combinations (MDT, MTQ, QDT) are also used in industry.

Basically silicones hold a hybrid position between organic and inorganic compounds, peculiar between silicates and organic polymers. Siloxane link (Si-O-Si), that are present in silicates, is liable for the “inorganic” character. Because of the direct link between silicon and carbon the organic properties arise. Silicone resins are manufactured by hydrolytic condensation of different silicone precursors.

#### **1.4.1 Silicone resin synthesis**

- *Muller-Rochow synthesis*

The initial point for manufacturing of silicone resins are chlorosilanes which are obtained on a large scale by the Muller-Rochow synthesis. In this, in fluidized bed reactor very pure silicon (>98%) is allowed to react at 280°C in the presence of catalysts and promoters with chemicals mainly methyl chloride or phenyl chloride.



Structure, processing, and complex properties of the silicone resins is determined by the the distribution and number of the structural units and the functional groups on the silicon atom.

#### **1.4.2 Properties of Silicone resin**

The properties of the silicone resin are the crucial reason for its wide application and commercial achievement.

- Weathering resistance
- Thermal stability
- At low temperatures its behave like elastic
- surface tension is low
- Hydrophobicity
- Surface activity
- Release and lubricating properties

Because of the above mentioned properties silicone resins and silicone combination resins extensively used in field like impregnation of polymeric resins and concrete, weather resistant exterior coatings or high-temperature resistant coatings. These binders are used in the form of solutions, emulsions and liquid resins.

There have been attempts to blend silicone resins with vinyl ester to improve its toughenability. Curing of the thermoset in the presence of rubber leads to its precipitation, which results in the formation of phase separated blends.<sup>[2]</sup> Moreover, specific disadvantages are suffered by blends having liquid rubber including low glass transition temperatures, high water absorption and reduced elastic modulus.

We hypothesised that preparing preformed silicone microspheres would enable proper dispersion of the rubber phase within the matrix. In view of the same, PDMS microspheres were prepared and used as a filler for vinyl ester resin. A brief introduction of microspheres is presented in the following section.

## **1.5. Silicone microspheres**

Microspheres are small spherical particles, having diameters in the micrometer range (mostly 1  $\mu\text{m}$  to 1000  $\mu\text{m}$  (1 mm)). Various natural and synthetic materials are generally used to prepare these microspheres. Microspheres made of glass, polymer and ceramic are commercially available.

Due to wide variations in density, solid and hollow microspheres are used for different applications. To lower the density of a material hollow microspheres are mainly used as additives. Solid microspheres have numerous applications based on the material they are constructed of and size they possess.

Microspheres produce a ball-bearing look which will impart finished products with an elegant silky texture, increased payoff, and enhanced slip because of their shape and size. The most common types of polymer microspheres are polyethylene, polystyrene, silicone and expandable microspheres. Silicone microspheres are primarily used in biomedical application because of their inertness against the biological environment as it do not show any immunogenic responses. Due to their high elastic, tensile, and compressive strength properties it can be used as modifier for other resin.



## 1.6. PDMS-Vinyl ester Core shell

To improve the compatibility of the silicone with the base vinyl ester resin, introduction of an additional layer of vinyl ester on the PDMS microspheres was done. The resultant microspheres were expected to possess a core shell morphology with an inner core of PDMS, coated with a shell of vinyl ester. This was achieved by suspension curing of the vinyl ester resin over the suspended elastomeric template of silicone (PDMS). Based on the required shell thickness (20 micron), the amount of vinyl ester resin was taken. A representative core shell morphology is presented in figure.

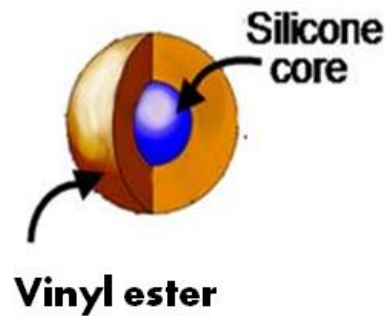


Figure 1.2: PDMS-Vinyl ester Core shell

## 1.7. Methods of preparation of microspheres

Different methods of preparation of microspheres are reported in the literature. Some of them are briefly discussed in following sections.

### 1.7.1. Suspension polymerization technique

Suspension polymerization is a type of heterogeneous radical polymerization process that uses mechanical agitation to mix a monomer or mixture of monomers in a liquid phase, such as water, while the monomers polymerize, forming spheres of polymer.

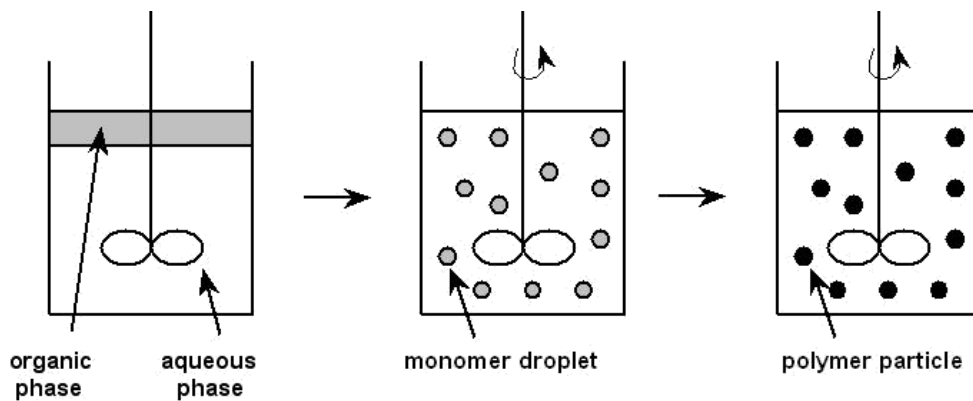
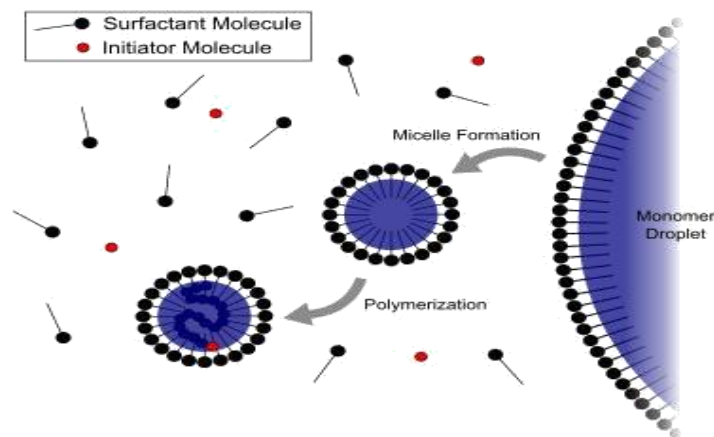


Figure 1.3: Schematic representation of Suspension polymerization

The reaction mixture consists of two phases, first phase is liquid matrix and the second consists of monomer droplets. The monomer and initiator do not solubilize in the liquid phase, so they form as droplets within the liquid matrix. Stabilization of the monomer is mainly done by addition of a suspension agent to droplets which hinders monomer droplets from coming together. The reaction mixture mainly has a volume ratio of monomer to liquid phase of 0.1 to 0.5. The liquid phase works as a heat transfer agent, permitting high rates of polymerization with small change in the temperature of the polymerizing solution. The reactions are usually carried out in a stirred tank reactor where the solution is continuously mixed using turbulent pressure or viscous shear forces. This stirring action aids in keeping the monomer droplets separated and helps in creating a more uniform suspension, which leads to a more narrow size distribution of the final polymer beads. This process of polymerization is generally performed till completion. Individual bead kinetics of the polymerization is similar to that of typical radical polymerization.

### 1.7.2. Emulsion polymerization technique

Emulsion polymerization is a type of heterogeneous radical polymerization which generally initiates with an emulsion incorporating water, monomer, and surfactant. Oil-in-water emulsion is the most common type of emulsion polymerization, in which droplets of monomer (the oil) are emulsified with surfactants in a continuous phase of water. Water-soluble polymers, like polyvinyl alcohols or hydroxyl ethyl celluloses, can be used to act as emulsifiers/stabilizers. Agitation and proper control of the emulsifiers / stabilizers are needed to keep the emulsion stable. Rather than occurring in emulsion droplets, polymerization takes place in the latex particles that form spontaneously in the first few minutes of the process. The size of latex particles is mainly 100 nm, and are comprised of many individual polymer chains. The particles are prevented from coagulating with each other because each particle is surrounded by the surfactant; the charge on the surfactant repels other particles electrostatically.



**Figure 1.4:** Formation of micelle during emulsion polymerization

## 1.8. Project aims and objectives

This project deals with a novel approach to toughening of vinyl ester thermoset by the use of elastomeric microspheres, such as silicone microspheres and core shell silicone- vinyl microspheres. The effect that these microspheres have on toughness of vinyl ester resin is an active area of research which motivated us to attempt the present work. Due to the elastomeric nature, it is expected that PDMS and core shell microsphere will act as impact modifier and provide flexibility to the polymeric matrix, and large amounts of energy is absorbed. The additional layer of vinyl ester as a shell onto core silicone microsphere helps to achieve better interfacial adhesion due to good compatibility between matrix and modifier. It is important here to understand that toughness depends to a high extent on the interfacial adhesion between the particle and matrix. Cured vinyl ester which is unmodified is brittle, and various thermoplastics, elastomers and fillers have been introduced with an aim to increase the energy absorption characteristics.

More specifically, the objectives of this research are:

- To synthesize and characterize PDMS microspheres and core shell PDMS/Vinyl ester microspheres.
- To prepare vinyl ester composites containing the developed microspheres.
- To investigate the effect of increasing loading of the fillers on the various properties such as mechanical, thermal and structural properties of the composites.

## CHAPTER 2

### EXPERIMENTAL

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#### 2.1. Introduction

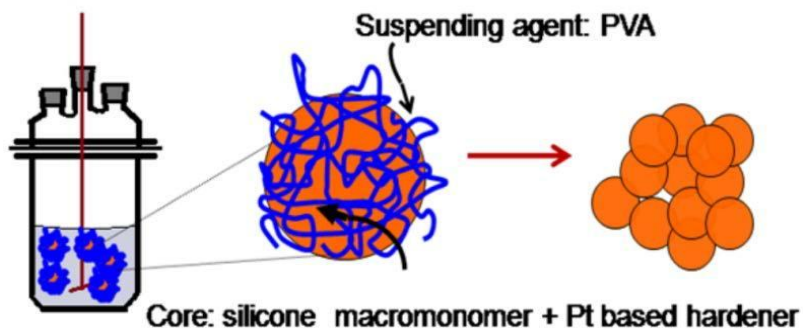
This section deals with the synthesis and characterization of PDMS and CSR microspheres as modifier for the toughening of vinyl ester. The details of their preparation as well as their composites with vinyl ester are also described.

#### 2.2. Materials

Silicone resin (Elastosil M4644) and the platinum based hardener was obtained from the Wacker, Germany. Vinyl ester (revex plasticizers, RPL 401 ( grade); styrene content 35%) initiator (MEKP) and accelerator (Cobalt Octoate) was used as received. PVA (Mol. wt. 14000, CDH) and chloroform (CDH) were used without any further purification. Distilled water used for the entire course of study.

#### 2.3. Preparation of siloxane microspheres

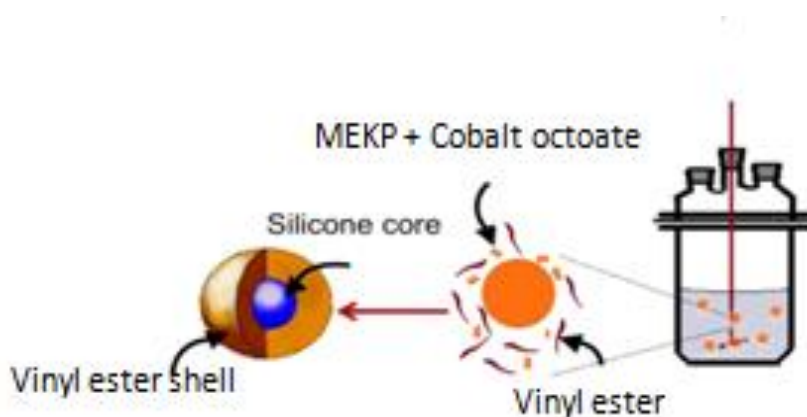
Suspension polymerization process is used to prepare the PDMS core. The silicon resin macromonomer was dissolved in chloroform in varying amounts (30-60% w/v) to which platinum based hardener (10:1:: resin : hardener) was added accordingly to prepare a feed solution. The curing was performed in 1 L four-necked reaction vessel, equipped with a nitrogen inlet tube, and a rubber septum by which the feeding is done with a hypodermic syringe. The reactor contained the suspending agent, PVA (1.5% w/v), which was left under continuous stirring (500-700 rpm) at 45°C. Further the polymerisation reaction was left to carry out for 8 h, after that the reaction mixture was allowed to cool and the microspheres were then filtered, washing of microspheres was done with water and then allowed to dried under vacuum at 80°C for 2 h. Conversion degree was measured gravimetrically which is equal to the ratio of mass of microspheres to the amount of macromonomer used during its preparation. The schematic of formation of oil in water silicone droplets during suspension polymerization are shown.



**Figure 2.1:** Oil in water silicone droplets formation during suspension polymerization

## 2.4. Preparation of core-shell PDMS

Vinyl ester were coated on the PDMS microspheres in a separate curing step. To fulfill this, the (5g) vinyl ester resin PDMS microspheres (10g) were added to PDMS microspheres (10g), and ultrasonication of mixture was done for 15-30 min which was done prior to adding stoichiometric amount of hardener. Subsequently, 5 ml of Tetrahydrofuran was added, and then, into a reactor, slurry was added which contained 1.5 L of PVA solution having 1.5% w/v and was stirred at 50 °C for 5 h to ensure complete curing of vinyl ester on the PDMS core. The schematic of PDMS templated vinyl ester curing process are shown .

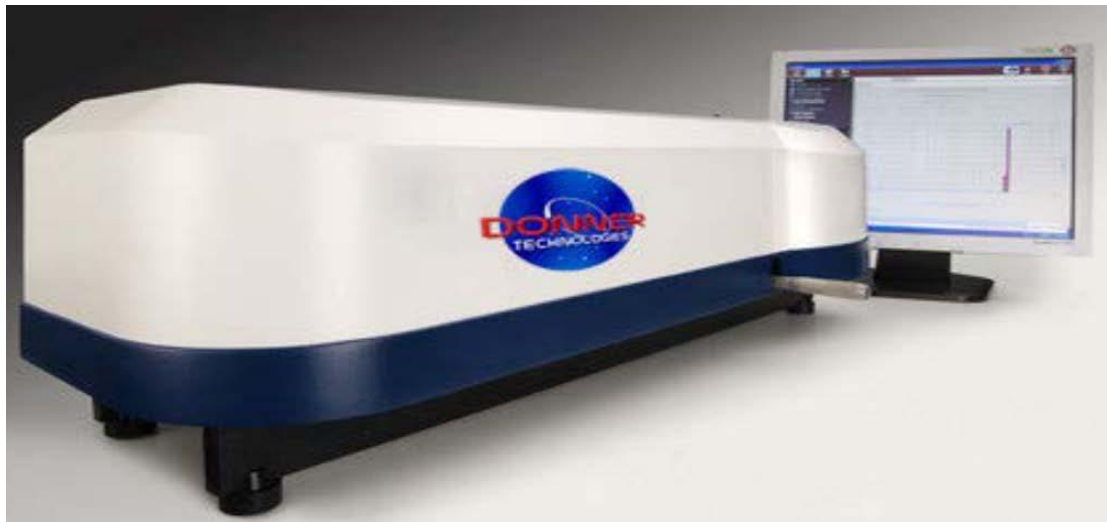


**Figure 2.2:** Schematic of PDMS templated vinyl ester curing process

## 2.5. Characterization

### 2.5.1. Analysis of Particle size

The particle size distribution of the microspheres both before and after vinyl ester coating was determined by a particle size analyser (DIPA 2000, Donner). The microspheres were suspended in distilled water by continuous stirring prior to laser based diffraction measurements.



**Figure2.3:** Particle size analyzer

### Principle

Functioning of the Laser particle size analyzer is as per the optic properties which is specific to laser such as collimation, monochromaticity and leads to diffraction and scattering very easily. When the beam is illuminated by the particles which are distributed in the liquid, the phenomenon of scattering & diffraction take place. The scattered or diffracted light is passed via Fourier lens which leads to a series of light rings and are produced on the focal plane. Its radius is relevant to the the particles size; the light's density is decided by particles numbers. Scattering and diffracted signals from the particles in different diameters are obtained by circular array of photo detectors on focal plane. Then the signals is transferred to the computer through A/D conversion or some different approach, Further processed in accordance to Fraunhofer diffraction or Mie scattering theory .Thus the particle size distribution of the sample is obtained.

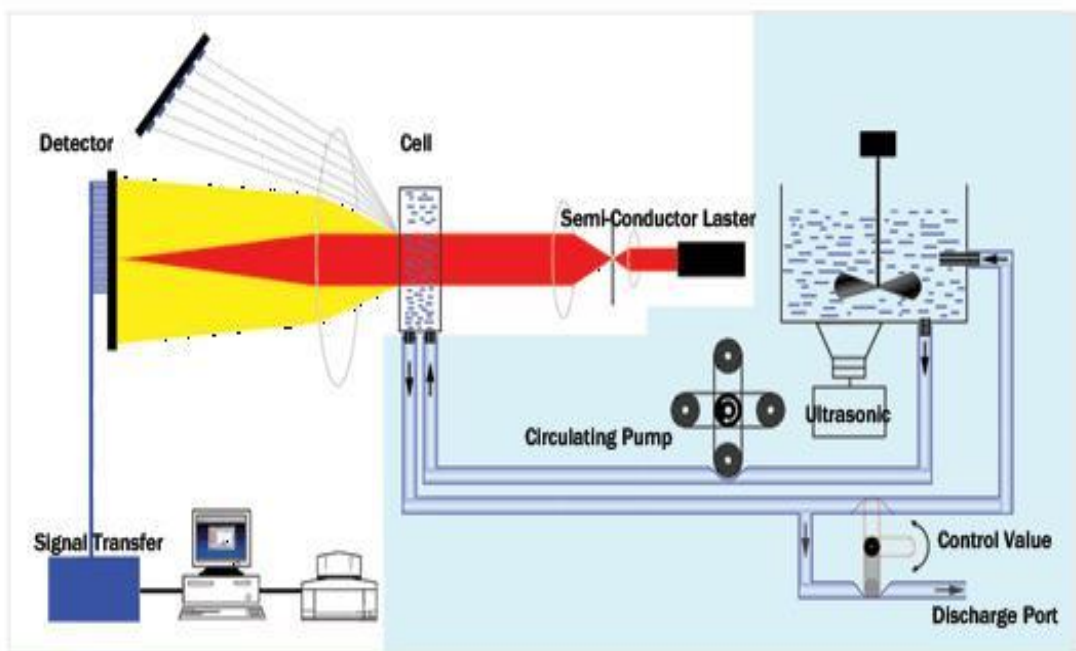
## Working and instrumentation

- **The laser channel** uses the laser obstruction time (LOT) principle for obtaining diameter of the particles when flow is dynamic. The rotating laser beam is temporarily blocked by the particles as particles pass through the analyzer. A detector measures the obstruction time of the individual particles in the laser beam.

As the data are being collected on single particle basis, high resolution results are obtained. Optical or physical properties do not influence the obstruction time. Or we can say, the particle size is independent of absorption, refractive index, porosity, electrical conductivity, surface texture or any other kind of the sample pre-knowledge.

- **The Video channel** evaluate the particles shape in dynamic flow. This channel is equipped with a CCD microscope video camera. A synchronized strobe light provides illumination, and then the displayed image is further analyzed.

The images are automatically processed and evaluated by means of image analysis software, and an array of size and shape parameters are analysed. Using this path, during a measurement cycle thousands of sampled images can be collected. Multiple types of graphs and tables are needed to present all the measurement results, and storage of sample image is done for evaluation for later time.

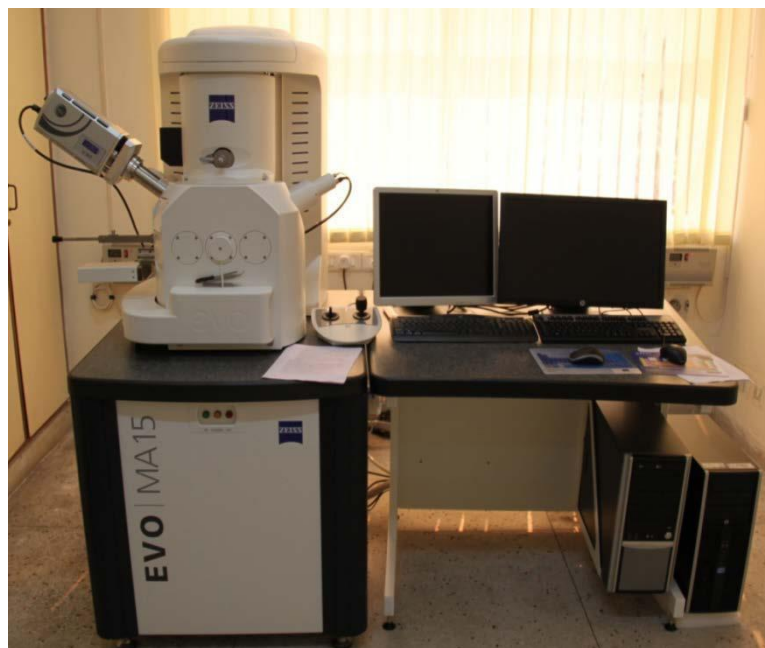


**Figure 2.4:** Schematic diagram of working of the particle size analyzer

### 2.5.2. Scanning electron microscopy

Scanning Electron Microscope (Zeiss EVO MA15) is used to study the surface morphology of samples supporting an acceleration voltage of 20 kV. Samples were kept on aluminium stubs and sputter- which ha been coated with gold and palladium (10 nm) by using a sputter coater (Quorum-SC7620) which was operating at 10-12 mA for 120 s .

For this purpose, vinyl ester coated microsphere is firstly cut with a sharp razor blade and then placed with care on a stub and sputter coated with gold. Then an energy dispersion analyser (EDS) is used to determine the elemental composition in the core and shell region.



**Figure 2.5:** Scanning electron microscope

#### **Principle:**

Accelerated electrons in an SEM carries significant amounts of kinetic energy, and this energy is decadent as a number of signals exhibit by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals comprise secondary electrons (which create SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to



determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for continuum X-rays and elemental analysis), heat and visible light(cathodoluminescence--CL).

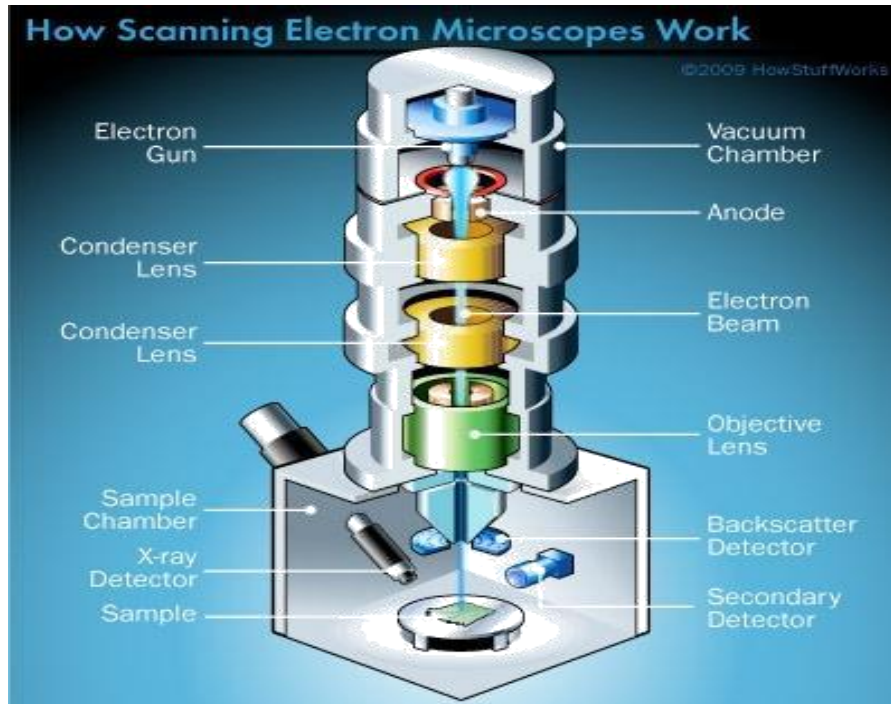
Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination).

### **Instrumentation:**

SEMs comprise of the following mandatory components:

- Electron Source ("Gun")
- Sample stage
- Electron Lenses
- Signals Detectors
- Display / Data output devices
- Infrastructure Requirements:
  - Power Supply
  - Cooling System
  - Vaccum system
  - Room free of ambient magnetic and electric fields
  - Vibration-free floor

SEMs must contain one detector (usually a secondary electron detector), and additional detectors are present in most of them. Particularly the specific capabilities of instrument are alarmingly depends on the detectors it accommodates.



**Figure 2.6:** Schematic diagram of the working of a scanning electron microscope

### 2.5.3. ATR-FTIR

FTIR spectra of samples were recorded in the wavelength range  $4000 - 600 \text{ cm}^{-1}$  using Fourier Transform Infrared (FTIR) spectroscopy on a Thermo Fisher FTIR (NICOLET 8700) analyser with an attenuated total reflectance (ATR) crystal accessory.



**Figure 2.7:** ATR-FTIR

#### **Principle**

An attenuated total reflection accessory function by measuring the changes which takes place in a totally internally reflected infrared beam when the beam comes in contact with a sample. An infrared beam with a high refractive index at a certain angle is focused onto an optically dense crystal. This internal reflectance generate an evanescent wave that reach ahead the surface of the crystal into the sample held in contact with the crystal. The generated evanescent wave can be compared with a bubble of infrared that settle on the surface of the crystal.

The evanescent wave which has generated project only a few microns ( $0.5 \mu - 5 \mu$ ) ahead the crystal surface and also through the sample. It should be noted that, there must be good contact between the crystal surface and the crystal sample. The location of the infrared spectrum where the sample incorporate energy, the evanescent wave will be reduced or re-altered. The reduced energy from each evanescent wave is send back again to the IR beam, which then vent the opposite end of the crystal and is passed through the detector in the IR spectrometer. An infrared spectrum is then generated by the system.

#### **2.5.4. Mechanical Characterization**

The mechanical properties of polymers are of great interest to scientists and relevant to industry. To study in detail the fundamental behaviour of these materials, analysis of high strain rate behaviour should be done. Properties of materials like deformation at high strain rates depend on molecular and atomic behaviour which may differ from that found at low rates. Better understanding of the high strain rate properties of these materials is given by the correlation between temperature and strain rate in both polymers and metals by relating them to quasi-static measurements. Better understanding of when these relationships do and do not hold would be especially useful for future research activities. Generally, the mechanical properties (strength and modulus) increase with increasing loading rate [38]. In order to determine the strain rate sensitivity of samples, three different types of studies are performed.

The basic principle of these tests are described in the following section

##### **2.5.4.1. Quasi static testing**

Quasi static loading refers to loading that have very low (almost negligible) inertial effects in solid mechanics. Or we can say time and inertial mass are insignificant. Quasi static testing are basically characterized by very low strain rate. The strain rate for the above said testing is in the range of  $10^{-3}$  to  $10^0 \text{ sec}^{-1}$ . Quasi static testing can be performed in either modes to evaluate the tensile, compression and flexural properties of the said material.



**Figure 2.8:** Universal Testing Machine (UTM)

### **Tensile Testing (ASTM D 638)**

The determination of mechanical properties like tensile modulus and strain-at-break were carried out as per ASTM method D 638 at ambient temperature using an International equipment Universal Testing System (3369). Dumb bell shaped specimens were prepared for tensile testing by mixing required amounts of vinyl ester, hardener and the different modifiers. The specimens used in the tensile testing is of dog-bone shaped which has dimensions 165 mm long, 3 mm thick and 13 mm wide across the centre of the casting for vinyl ester resin. During the tensile tests the samples were subjected to a cross head speed of 50 mm/min. To obtain the effective average value of tensile properties testing of three specimens were done at least.



**Figure 2.9:** Photographs of samples a) Microspheres reinforced vinyl ester b) neat Vinyl ester

**Flexural testing (ASTM D 790)**

Three point single edge notch bending mode is used for performing Notched flexural testing of the samples. To fulfill this, specimens of requisite dimensions (127 mm length x 12.5 mm width x 3.5 mm thickness and 3 mm notch) were framed and while maintaining 60 mm span length the samples were subjected to a deformation rate of 2 mm/min. The obtained data was evaluated to determine the mode I fracture toughness ( $K_{Ic}$ ) of the samples as per the following equation: [34]

$$K_{Ic} = \frac{3 \times P \times L \times a^{1/2}}{2 \times B \times w^2} Y\left(\frac{a}{w}\right) \dots\dots\dots(1)$$

Where, B, P and L refer to sample thickness, load at break and span length.

respectively. The geometry factor,  $Y\left(\frac{a}{w}\right)$ , is calculated as per the formula below,

here w is width of sample and a is notch length .

$$Y\left(\frac{a}{w}\right) = 1.93 - 3.07 \times \left(\frac{a}{w}\right) + 14.53 \times \left(\frac{a}{w}\right)^2 - 25.11 \times \left(\frac{a}{w}\right)^3 + 25.8 \times \left(\frac{a}{w}\right)^4 \dots\dots\dots(2)$$



**Figure 2.10:** Photographs of samples a) neat Vinyl ester b) Microspheres filled vinyl ester

#### **2.5.4.2. Low velocity Impact testing**

Low velocity testing are the basically characterized by intermediate strain rate. The strain rate for the above said testing are in the range of  $10^0$  to  $10^3 \text{ sec}^{-1}$ . Low velocity testing is done to evaluate the behaviour of the material under sudden impact and can be used to determine the material toughness of the polymeric material.

#### **Izod Impact testing (ASTM D 4812)**

The izod impact test is a dynamic test in which a test piece U-notched or V-notched in the middle and supported at each end, is broken by a single blow of a freely swinging pendulum (Fig.2.12). The energy absorbed is then measured. The impact strength of material is measured by this absorbed energy. For this purpose, specimens of requisite dimensions (127 mm length x 12.5 mm width x 3.5 mm thickness and 2.25 mm notch) were prepared and put to deformation.



**Figure 2.11:** Impact testing machine



**Figure 2.12:** Photographs of samples a) neat Vinyl ester b) Microspheres reinforced vinyl ester



## 2.6. Preparation of vinyl ester composites

Toughened vinyl ester composites containing different composition of both coated and uncoated microspheres (1-7%) w/w were prepared by adding required amounts into the vinyl ester resin which is then proceed by ultrasonication of the resulting mixture for 30 min at 33 kHz. To fulfill this, the microspheres were sieved using a 40/100 mesh and the particles between the particle size 250 to 177  $\mu$  were collected for the use as filler. (MEKP (initiator), Cobalt Octoate (accelerator)) was subsequently added to the mixture (2%), and further ultrasonication is carried for another 15 minutes to get rid of any air bubbles that had been entrapped. Under vacuum the suspensions were allowed to degassed and then transferred to greased cylindrical stainless steel molds, and then the reaction are kept for 24 h at 30°C for curing. Same procedure were followed for preparation of neat vinyl ester specimens and the detail data of all the compositions prepared are mentioned in Table 1. The samples has been represented as VE followed by the concentration of microspheres and the type of microsphere used for its preparation, i.e. ‘R’ represents uncoated PDMS microsphere and ‘CSR’ represents vinyl ester coated core shell microspheres with PDMS core.

**Table 1:** Sample designation and compositional details

Sample designation	Unsaturated polyester (g)	Initiator (MEKP)	Accelerator (cobalt octoate)	Microspheres
VE	100	2 g	2 g	–
VE1x	100	2 g	2 g	1.04 g
VE3x	100	2 g	2 g	3.12 g
VE5x	100	2 g	2 g	5.20 g
VE7x	100	2 g	2 g	7.28 g

## CHAPTER 3

### RESULTS AND DISCUSSION

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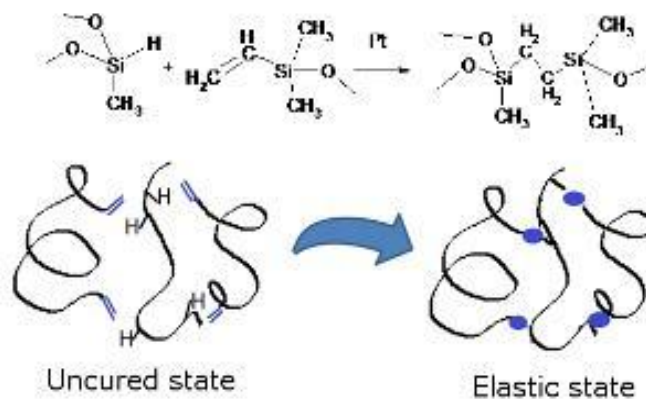
This project deals with an approach to improve the energy absorption characteristics of vinyl ester thermosets. Several methods have been employed for toughening vinyl ester resins, the most successful being the introduction of preformed elastomeric microspheres, where small loadings can lead to remarkable improvement in the fracture properties.

In the present study, we have prepared PDMS core- vinyl ester shell microspheres by suspension polymerization process, with an approach to enhance the compatibility between the vinyl ester resin and preformed elastomer. The effect on mechanical and thermal properties due to importing the rubbers has been evaluated.

#### 3.1. Suspension curing of siloxane

Suspension polymerization is one of the most simple techniques used for preparation of spherical beads, wherein the separate monomer phase is stabilised by the combined action of surfactant and mechanical agitation. Other important parameters include the temperature of the reaction medium, which in turn is decided by the type of initiator employed for polymerisation reaction. Here in our work, the vinyl terminated methyl hydrosiloxane-dimethylsiloxane copolymer in the presence of a platinum based hydrosilylationcatalyst[35] was cured at 45°C as per reaction scheme 2. As can be seen, the reaction between Si-H bonds and the vinyl groups of the polymer is catalysed by the presence of a platinum based catalyst resulting in the formation of a three dimensional cross linked network.

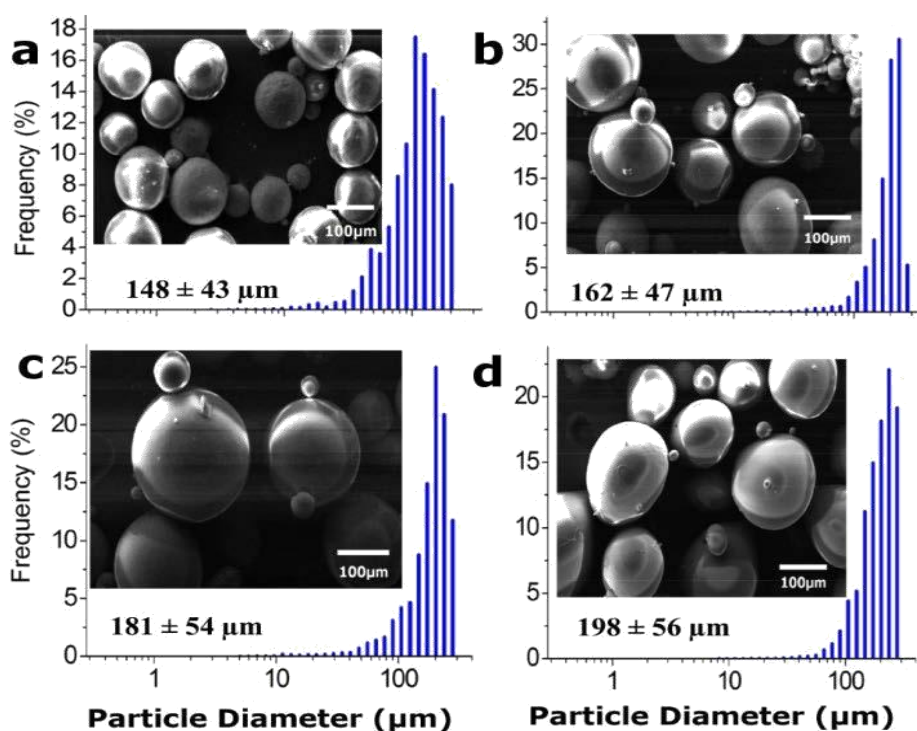
Unlike peroxide-curing, platinum-catalyzed addition reactions do not produce odour or flavour impairing by-products, thereby increasing the application of these materials in biomedical fields. The rate of curing can be controlled by varying the temperature of the media, which was maintained at 45°C for the present work.



**Scheme 2:** Platinum catalysed hydrosilylation of silicone.

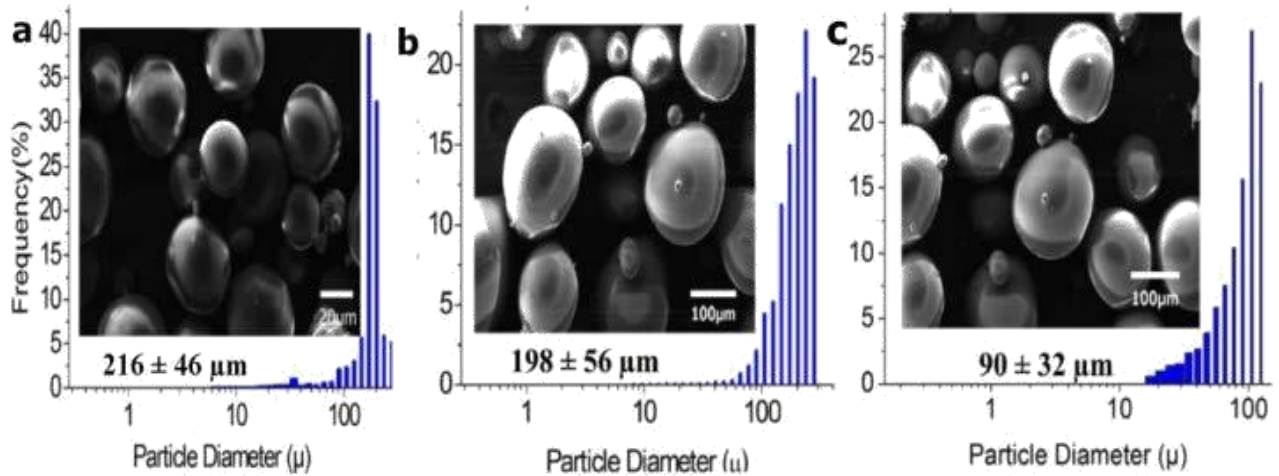
### 3.2. Concentration effect on particle size

Figure 3.1 presents the consequence on the particle size distribution of the resultant microspheres because of increasing feed macromonomer solution concentration. As is evident from the figure, on increasing the concentration of siloxane in the feed the distribution move close to larger sized microspheres. This can be associated to the increased polymerisable content in the hydrophobic dispersed droplets. The smooth texture of the PDMS surface (Figure 1, Inset) was studied by Morphological investigations. It is to be noted that under the reaction conditions maintained during the present work, it is evidenced by gravimetric analysis that almost complete conversion (> 98%) could be achieved.



**Figure 3.1:** Effect of feed concentration on the particle size distribution and surface morphology of PDMS microspheres (stirring speed 600 rpm). a) 30% b) 40% c) 50% d) 60%

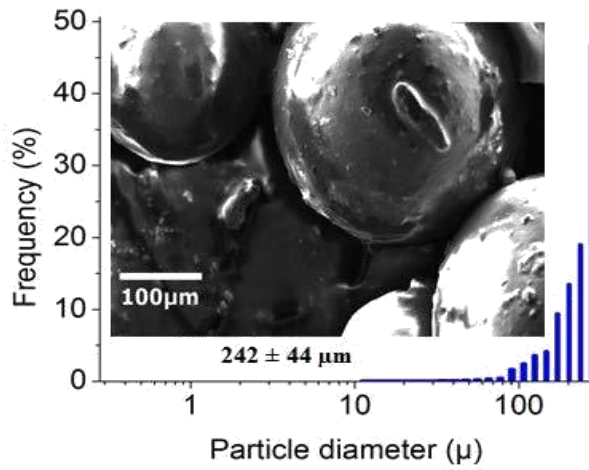
The on the particle size distribution of the microsphere due to varying stirring speed was also studied and these results are presented in Figure 3.2, (feed concentration 60 % w/v). It is observed that particle size distribution shifts towards lower size as the stirring speed is increased, which could be associated with the fact that shearing of the large oily droplets took place into smaller microspheres, which even at high stirring speed can be stabilised in the presence of surfactant.



**Figure 3.2:** Effect of stirring speed on the particle size distribution and surfacemorphology of PDMS microspheres. a) 500 rpm b) 600 rpm c) 700 rpm

### 3.3. Effect of coating on microsphere dimensions and morphology

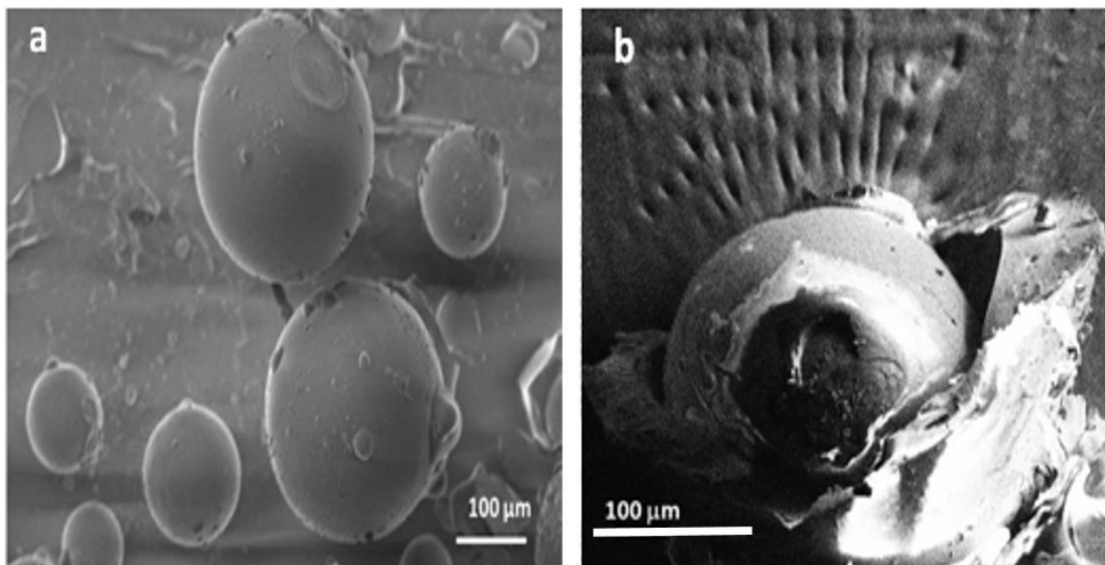
With an approach for improve the compatibility of the elastomeric microspheres with the thermosetting resin, coating of the microspheres with a layer of vinyl ester has been carried separately. As expected, the particle dimensions increases due to coating of PDMS microspheres, which was determined by particle size analysis. As a representative case, the size distribution of core shell PDMS –vinyl ester microspheres prepared as per 60 % w/v siloxane in the feed is presented in Figure 3.3. Comparison with the distribution pattern of uncoated PDMS reveals that the thickness of coating is of the order of 20  $\mu$ . Significantly, the surface of the coated microspheres was found to be rather rough in comparison to that of neat PDMS.



**Figure 3.3:** Particle size distribution and surface morphology of coated microspheres

### 3.3.1 Preparation and characterization

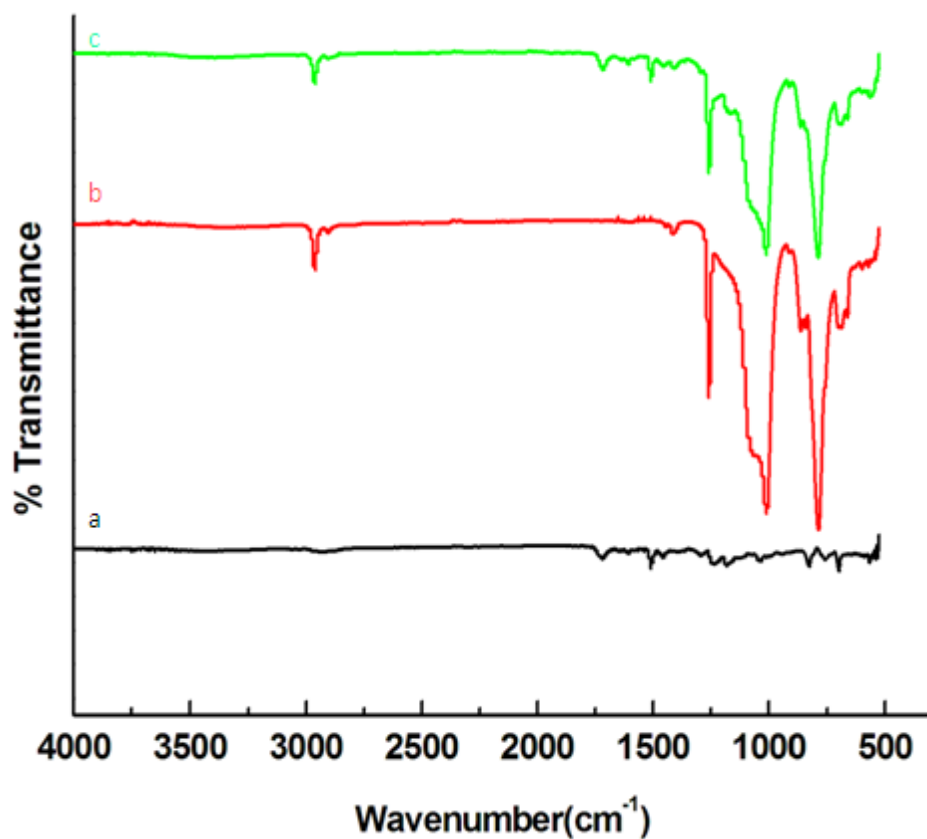
Vinyl ester resin - elastomeric PDMS composites were prepared and the energy absorption characteristic of these polymer composites was investigated using various mechanical testing methods. The SEM images of VE coated microspheres and cut cross section of the same are also presented in Figure 3.4, the same was introduced in the vinyl ester resin matrix after ultrasonication to ensure homogenous dispersion.



**Fig 3.4 :**SEM image a) VE coated PDMS microspheres b) Cut cross section of coated microsphere (VECR)

### 3.4. Structural properties

The FTIR of the PDMS, both before and after vinyl ester coating is presented in Figure 3.5. In the FTIR spectra of PDMS, we observe characteristic absorption peaks at  $802$  and  $1258\text{cm}^{-1}$  which could be associated to the  $(\text{CH}_3)_2\text{SiO}$  group vibration in the polymer.[11] Also a broad absorption at  $1000\text{-}1130\text{cm}^{-1}$  was also observed, which is due to the Si-O-Si vibration. An additional absorption bands at  $1607\text{cm}^{-1}$  can be seen due to vinyl coated microspheres which suggests the presence of vinylic double bond [12]. Appearance of additional absorption at  $1716\text{cm}^{-1}$  due to ester carbonyl stretching in addition confirms the coating of vinyl ester on the PDMS surface.



**Figure 3.5:** FTIR spectra of (a) neat vinyl ester (b) PDMS (c) VE coated PDMS

### **3.5. Vinyl ester -PDMS composites**

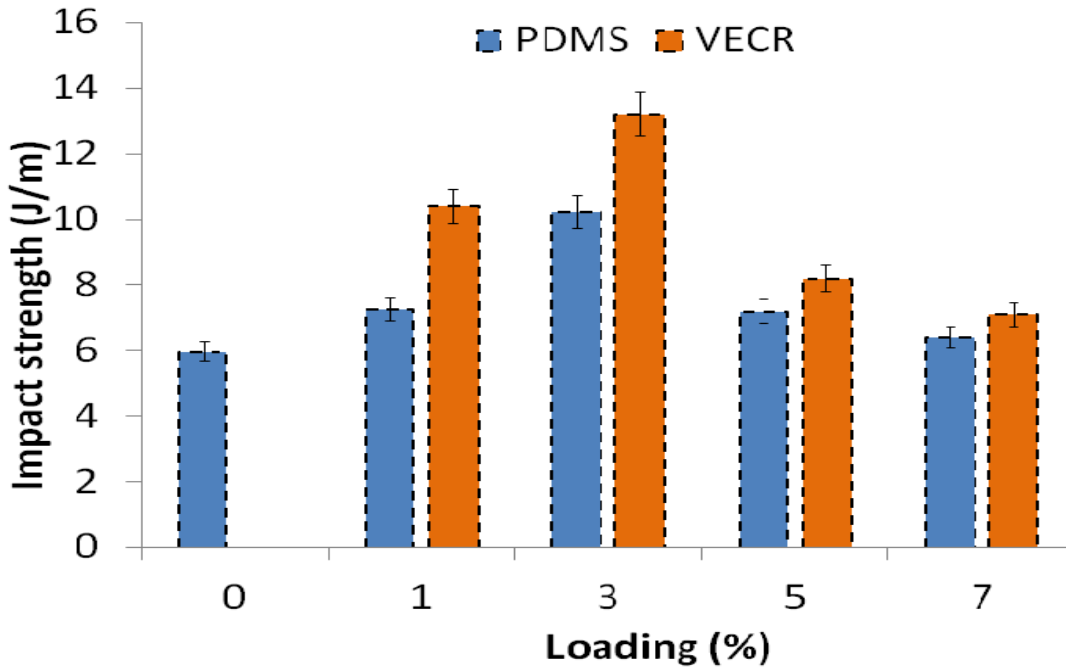
Composites of vinyl ester containing both PDMS microsphere and core-shell microspheres were prepared by dispersing them respectively into the resin with the help of ultrasonication and then it is proceed by curing with the platinum hardener in requisite ratio. Cured polymer was evaluated for its mechanical and thermal properties.

#### **3.5.1. Mechanical properties**

##### **3.5.1.1. Impact strength**

The introduction of elastomeric microspheres has brought a noticeable advancement in the impact strength of vinyl ester, as is clear from figure 3.5. The izod impact strength increased from 5.8 Jm<sup>-1</sup>(neat Vinyl ester) to 13.5 Jm<sup>-1</sup> (~132 % increase) on addition of 3 % w/w CSR. Comparable increase in the toughness have been reported earlier at such low loadings. [36] When uncoated PDMS was used as the filler the improvement in impact strength was less pronounced as compared to coated PDMS.

There are two major criteria for the elastomeric microspheres in order to display probable potential as impact modifiers for vinyl ester resin. Firstly, the microspheres should not agglomerate and exist as a well separated phase within the matrix. In addition, they should also exhibit strong adhesion with the base matrix. It appears that the superficial vinyl ester shell of the CSR highly interacts during the curing process with the vinyl ester, which results in improved dispersion in comparison to its uncoated counterpart. However, with increased loadings, the impact strength decreased, which can be attributed to the agglomeration of these microspheres.

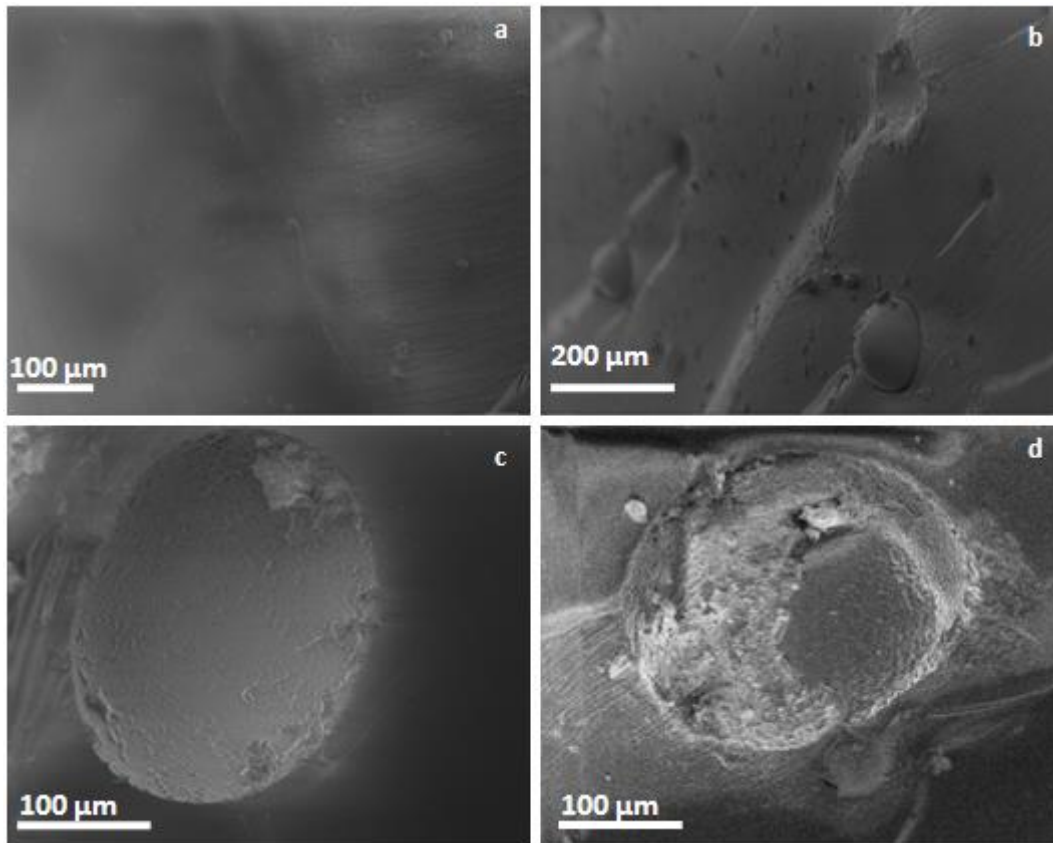


**Figure3.6:** Effect of elastomeric microspheres on impact strength of vinyl ester

Study of morphology of the fractured surface was carried out by SEM imaging and the results are depicted in figure3.7. It should be noted that, the fractured surface of vinyl ester is smooth and continuous and shows no symptom of plastic deformation, which shows typically brittle nature of thermoset polymer.[37]

In context to comparison, the surface of the fractured composite is quite rough. [28, 38, 39] It is interesting to note that when neat PDMS is employed as a filler, the microspheres are removed in the entirety. In contrast, broken microspheres were found to be embedded along the surface of fractured composites which consist of CSR. The existence of silicone rubber within the broken microspheres presents a direct confirmation of improved adhesion between the elastomeric phase and the vinyl ester matrix.





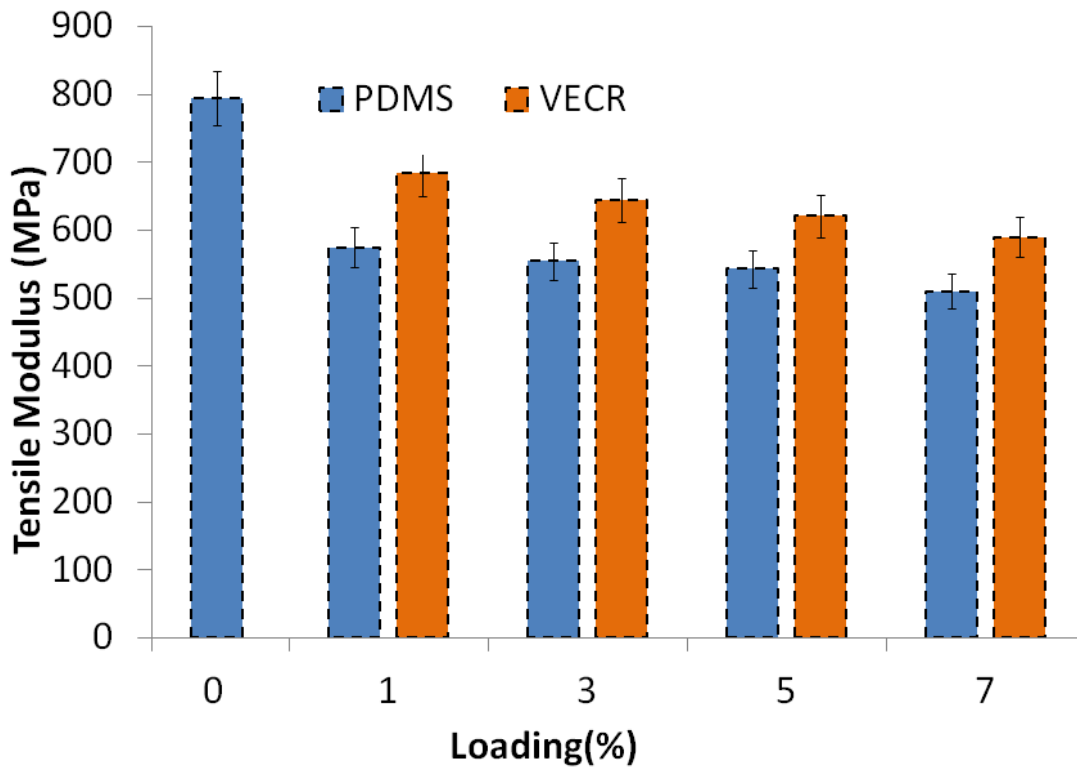
**Fig3.7:** SEM image of the fractured surface of a) neat VE, b) VE composite containing 3 % PDMS c–d )VE composite containing 3 % CSR.

Although the mechanism behind vinyl ester toughening in the presence of elastomers is not fully explicated, it is more or less accepted that the cavitation of rubber is responsible for the improved energy absorption in toughened compositions. [18, 37, 40, 41] On being subjected to a dynamic load, a tri-axial tension creates around the crack tip and the rubber particles tend to cavitate, which in turn mitigates the in-plane strain ahead of the crack thus minimized crack to propagate. Moreover, these small and evenly dispersed microspheres also tend to act as crack terminators.

### 3.5.1.2. Quasi-static testing

Figure 3.8 represents mechanical properties variations of the vinyl ester composites containing both neat PDMS as well as core shell PDMS-vinyl ester microspheres. The tensile modulus decrease on introduction of elastomeric microspheres, the amount of which was found to be proportional to the extent of loading. This can be explained on the basis of the elastomeric nature of PDMS which do not contribute to the mechanical strength of the composite material. [42].

It has been mentioned that in comparison to acrylate based elastomer, mechanical modulus loss is less pronounced when silicones are occupied as toughening agents. (Voo, Mariatti et al. 2012), and this is one of the reasons for advocating the use of silicones as toughening agents in thermosets for high end applications. The presence of vinyl ester coating in CSR seems to play a key role in maintaining the property of the base resin, as the uncoated silicones led to more pronounced decrease in the mechanical properties even at low loadings.

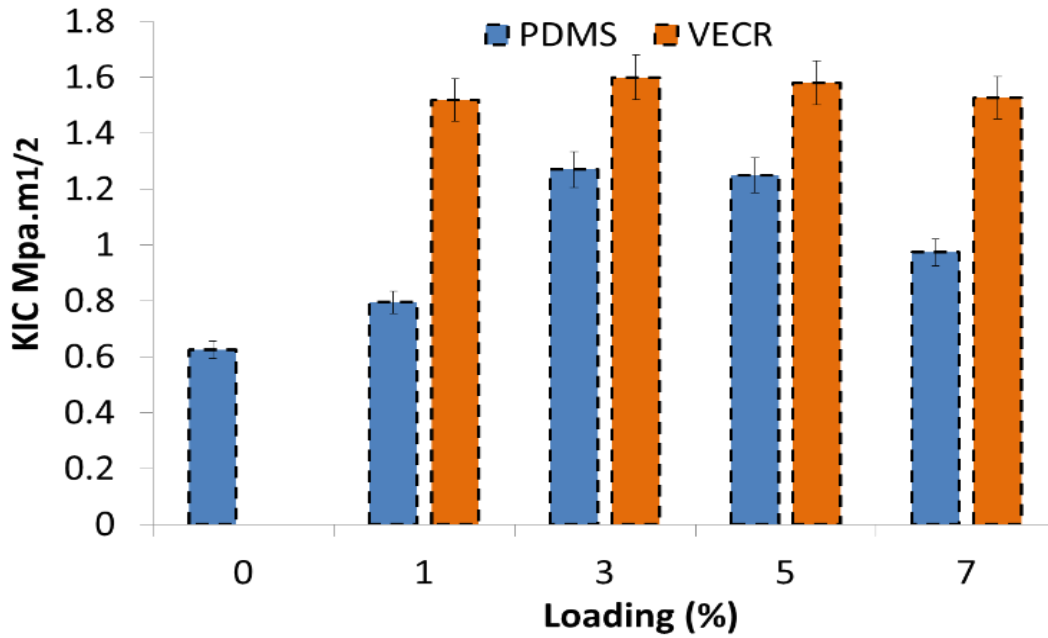


**Figure 3.8:** Effect of microsphere loading on mechanical properties of vinyl ester on Tensile modulus

### 3.5.1.3. Fracture toughness

Flexural three point bending tests were also performed on selected specimens, and the effect of notch on the mechanical response of the blend is presented in Figure 3.8. As expected, the introduction of elastomeric microspheres within the vinyl ester matrix led to an increased flexural strain, which can be attributed to the high extensibility of the rubbery domain. Most preferably, the core shell PDMS-vinyl ester could be flexed to a higher intensity, which in turn reflected in larger values of fracture toughness (KIC). The formation of notch results in lowering the flexural strength of specimens, which can be associated to the concentration of stress around the notch, further which leads to local yielding

followed by initiation of cracks is presented in Figure 3.8 represents the comparison of the fracture toughness ( $K_{Ic}$ ) as a function of composition type. The Mode I fracture toughness of vinyl ester increased by ~166% in blends containing CSR, indicates its potential towards improving the notch sensitivity of vinyl ester.



**Figure 3.9:** Effect of elastomeric microsphere loading on the fracture toughness ( $K_{Ic}$ ) of vinyl ester

## CHAPTER 4

### Summary and conclusion

Core-shell PDMS vinyl ester microspheres were prepared for its application as impact modifier in addition with thermosetting polymer such as vinyl ester resin. Suspension polymerization process is used to prepare core elastomeric beads of PDMS microspheres followed by addition reaction of silicone macromonomer in the presence of a platinum based hydrosilylation catalyst. Effect of operating parameters like feed concentration and stirring speed on the particle size distribution of resultant microspheres was studied to monitored at optimum conditions. To prepare core shell rubbers, microspheres were later coated with an vinyl ester layer in a separate step, so as to improve its compatibility with the vinyl ester thermoset. For preparation of toughened composites(1-7% w/w), both uncoated and vinyl ester coated PDMS microspheres were dispersed in the matrix of vinyl ester . Mechanical properties (both quasi static and dynamic) were studied to investigate the impact after addition of fillers. It seems that the presence of superficial vinyl ester coating on the elastomeric core plays an important role in the dispersion of the microspheres, which can be proved by the analysis of mechanical properties. The investigated izod impact strength increased by ~132 % on addition of 3 % core shell PDMS-vinyl ester.

## **RECOMMENDATIONS FOR FUTURE WORK**

The results obtained so far indicate that significant improvement in the tougheneability of vinyl ester resins can be brought about by introduction of elastomeric silicone microspheres. The compatibility with the matrix could be improved by the usages of its core shell analogue. However, due to time constraints, the behaviour of the composite under dynamic impact loadings could not be determined. In the future, the following studies need to be performed.

- Dynamic behaviour detailed studied of vinyl ester composites is required to be carried out over a range of temperature and frequencies including dynamic mechanical analysis.
- Quasi static compression tests should be performed to evaluate the response of the material under compressive load.
- High strain rate testing of samples using split Hopkinson pressure bar.
- Shock tube testing of the composites to investigate the behaviour of the material under blast loads

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