

Core shell Poly (dimethylsiloxane) - epoxy microsphere as impact modifier for epoxy thermosets

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CERTIFICATE

This is to certify that the M.Tech major project entitled “**Core shell Poly (dimethylsiloxane) - epoxy microsphere as impact modifier for epoxy thermosets**” has been submitted by NAHID IQBAL, for the award of the degree of “Master of Technology” in Polymer Technology is a record of bonafide work carried out by him. Nahid has worked under our guidance and supervision and fulfilled the requirements for the submission of the thesis. The project work has been carried out during the session 2012-2013.

To the best of our knowledge and belief the content therein is his own original work and has not been submitted to any other university or institute for the award of any degree or diploma.

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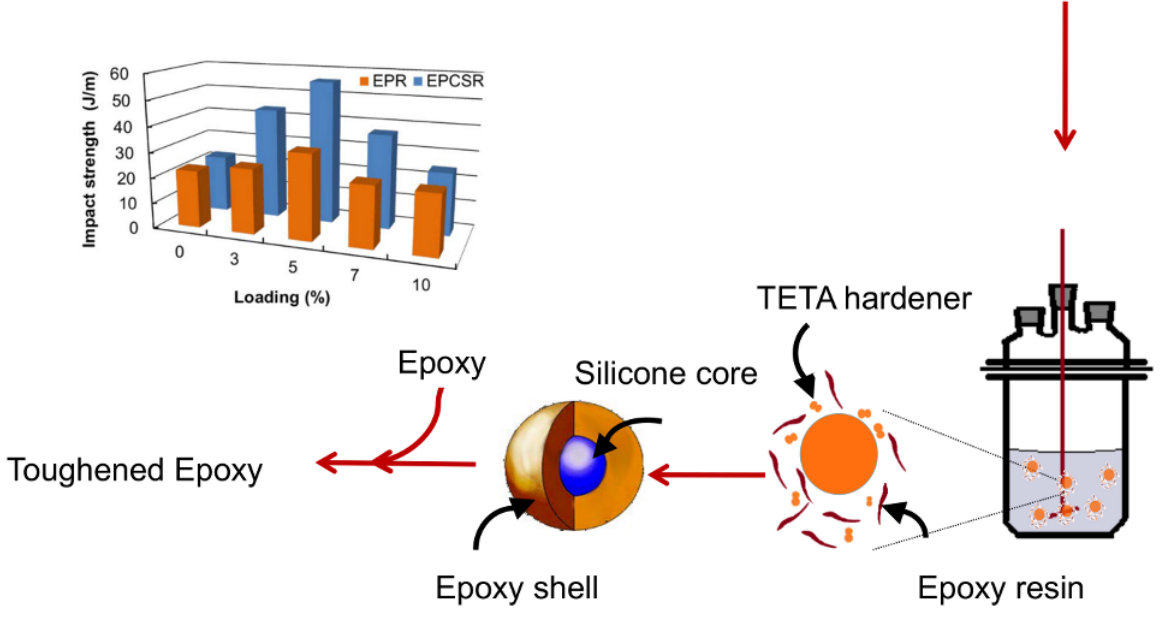
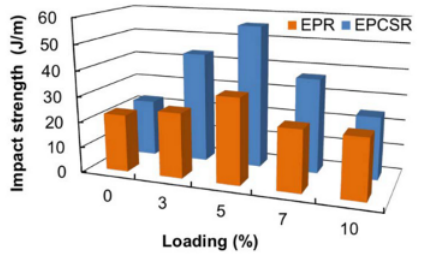
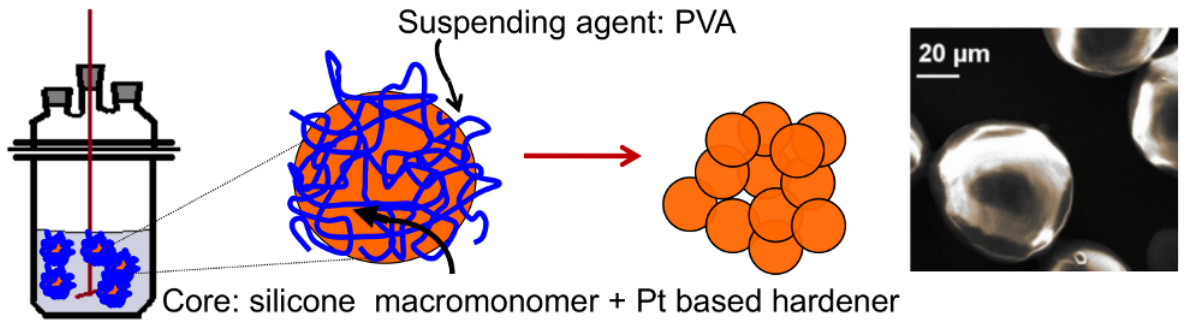
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Abstract

We report a two-step method for preparation of core shell elastomeric microspheres (CSR) by suspension polymerisation route and demonstrate its potential as an effective impact modifier for thermosetting epoxy resin. The first step involves suspension addition curing of siloxane macromonomer in the presence of platinum based hydrosilylation catalyst. The effect of reaction parameters on the particle size distribution was determined and the elastomeric microspheres were subsequently coated to prepare core-shell (PDMS-epoxy) microspheres. Epoxy composites containing varying amounts of microspheres (3-10 % w/w) were prepared and the effect of coating on the mechanical properties, both in terms of quasi-static as well as dynamic properties were evaluated. The mechanical properties were found to improve at low loadings (≤ 5 % w/w), and the presence of an epoxy coating on the PDMS in the CSR led to improved dispersion, which was evident from its improved mechanical properties. The Charpy impact strength increased by 148 % on introduction of core shell PDMS - epoxy (5% 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 the elastomeric phase and the epoxy matrix. A representative schematic of the entire process is shown in figure below.



CHAPTER 1

INTRODUCTION AND LITERATURE SURVEY

1. Introduction

The emergence of polymeric materials has changed the face of science and engineering immensely. 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 epoxy 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 epoxy.

The following subsections bring out the efforts, which have been directed towards improving the toughenability of thermosetting resins, particularly epoxy. The most common route is blending with suitable materials, which improves the properties of the base resin at relatively low costs compared to synthesizing new polymers. ^[1] The

details of the processes commonly employed for toughening of epoxy is mentioned under section 1.3.

In this context, the oldest method to improve the fracture properties of epoxy includes blending of the resin with liquid reactive rubbers.^[2] Curing of the thermoset in the presence of rubber leads to its precipitation, resulting in the formation of phase separated blends. However, blends with liquid rubber suffer from specific disadvantages including reduced elastic modulus, low glass transition temperatures and high water absorption. These issues can be overcome by using thermoplastics as toughening agents, which has become more common in the last few years.^[3, 4] However, most of the heat resistant thermoplastic modifiers are rather difficult to process. The fracture energy of toughened epoxy is generally proportional to its volume fraction, with the upper limit being of the order of 0.2-0.3.^[5] Further increase in loading leads to phase inversion, which in turn reflects in terms of reduced mechanical properties.^[6]

It is to be noted that irrespective of the type of polymer used for epoxy 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 the phase separation process is hindered leading to minimal improvement in the properties. In view of the 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 epoxy is the 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 the thermodynamic and kinetic factors during the curing process, which permits proper control over the resultant

morphology, thereby leading to larger improvements at much lower loadings.^[11] 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 majority of the relevant literature is, however, confined to core-shell particles in which the elastomeric core is obtained from organic rubbers, which are not heat resistant, thereby limiting its use to less demanding application.^[12, 13] In this context, the use of a thermally stable elastomeric core, e.g. silicone offers a potential solution.^[14-16]

Particle dimensions of the elastomeric filler is one of the most important parameters which affect its toughening ability. The effect of particle size on the fracture properties of epoxy has been extensively investigated, which indicate that the particles should be large enough to allow their deformation energy to be higher than their interfacial bonding to the epoxy matrix, else cavitation will not take place.^{[11, 17][18]} It has been reported that 100-200 μm diameter rubbers are the most efficient impact modifiers, which have reportedly led to over a tenfold improvement in the mechanical properties^[2]. At present, elastomeric microspheres for the purpose of epoxy toughening are synthesised by emulsion polymerisation technique, but very few papers describe the synthesis of such materials in the open literature.^[13, 19, 20] We hypothesise that elastomeric particles of these dimensions can be obtained by suspension polymerisation route, and the microsphere dimensions can be easily controlled by varying parameters like stirring speed and concentration of the feed solution. The aim of this work was to improve the properties of epoxy resins by blending with preformed siloxane elastomeric microspheres. Our approach was to synthesise core-shell poly (dimethyl siloxane) (PDMS) microspheres by a simple

suspension polymerization technique followed by coating with a layer of epoxy, which would lead to its apt dispersion within the thermoset.

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

1.1. Thermosetting epoxy resins

Epoxy compounds are one of the most important classes of thermosetting polymers.

The resin network has many desirable properties which include high tensile strength, excellent chemical and corrosion resistance and good dimensional stability[21, 22].

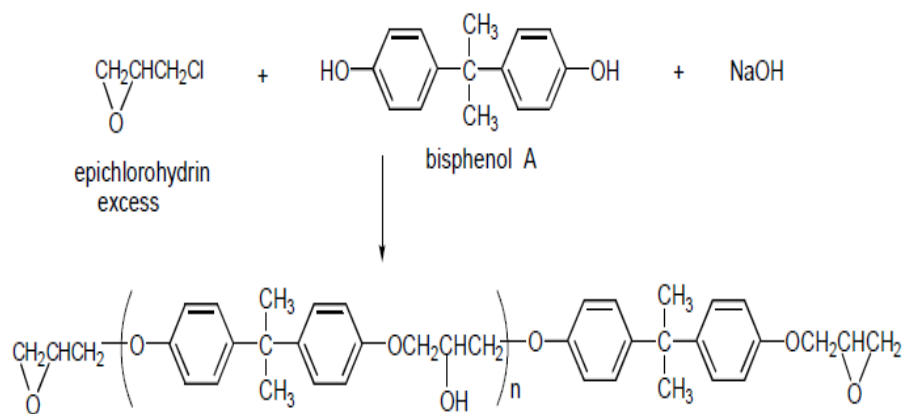
As a result, these materials are widely used for applications such as coating structural adhesives, reinforced particles and matrix for advanced composite materials[23-25].

Polyepoxide, known commonly as “epoxy” is a thermosetting polymer formed a result of reaction between an epoxide "resin" with polyamine "hardener".

Commercial epoxy resins contain aliphatic, cycloaliphatic or aromatic backbones.

They are prepared from either epichlorohydrin or by direct epoxidation of olefins with peracids. The most important intermediate for epoxy resins is the diglycidyl

ether of bisphenol A (DGEBA), which is synthesized from bisphenol A and excess epichlorohydrin as per shown in the scheme 1.



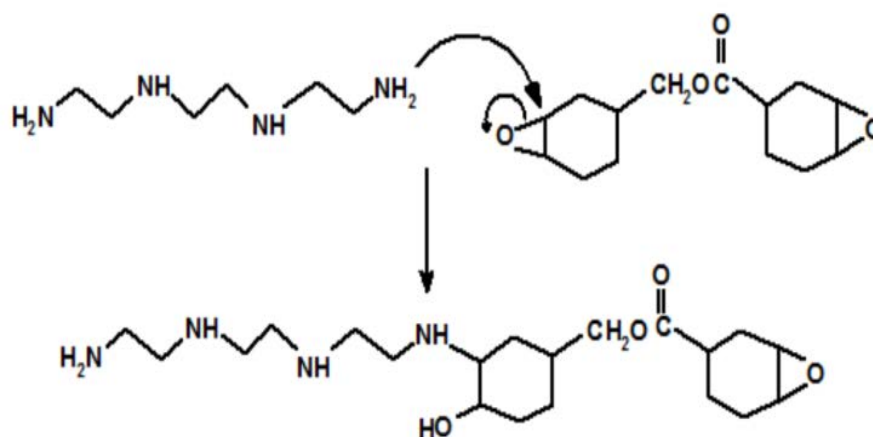
Scheme 1: Synthesis of diglycidyl ether of bisphenol A (DGEBA)

The epoxide ring can react with chemicals with different structures, especially those that have activated hydrogen atoms such as alcohols, amines and carboxylic acids, to mention a few. Treatment of epoxy resins with these agents results in formation of three dimensionally insoluble and infusible networks. The choice of curing agents depends on the required physical and chemical properties, processing methods and curing conditions which are desired. Epoxy resins can be cured with either catalytic or co-reactive curing agents who function as initiators for epoxy ring-opening homopolymerization.

Among chemicals which have the potential to act as curing agents, the primary and secondary amines are the ones which are most commonly employed. Primary amine functionality reacts with an epoxy group to produce a secondary amine and a secondary alcohol. The secondary amine can further react with an epoxy group to form a tertiary amine. Commercial hardeners generally consists of polyamine monomers, a typical example being triethylenetetramine (TETA). Each amine functionality can react with an epoxide group, so that the resulting polymer is heavily cross linked, and results in a formation of a rigid and strong structure. For the present study, a cycloaliphatic epoxy resin was chosen due to its potential

applicability in different areas and more importantly its UV stability, in view of the absence of light absorbing phenyl rings.

A reaction scheme representing the reaction between the primary amine functionality of TETA with epoxy group is shown in Scheme 2.



Scheme 2: Reaction scheme of primary amine of TETA with epoxy group of cycloaliphatic epoxy resin

This process is also referred to as "curing", and can be controlled through proper choice of temperature, type of resin and hardener, and the ratio of said compounds. The curing process, which is exothermic, can take minutes to hours for completion. Some formulations benefit from heating during the cure period, whereas others require time and ambient temperatures.

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. Flexible soft materials that can undergo energy-absorbing molecular rearrangements during deformation are tough, but have less tensile strength. In contrast, rigid hard materials are stiff but also very brittle having little ability to absorb energy, so their toughness

is low. To be strong and tough, a material must be able to absorb a large amount of energy during mechanical deformation, without sacrificing its stiffness. 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 epoxy resin is referred to as an “impact modifier”. The area under the stress-strain curve is often used to quantify toughness. Unmodified cured epoxy is inherently brittle and has low shrinkage and high creep resistance, which restrict their applications in areas which require high impact fracture strength, or even 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 effective route, but a major drawback is the decrease 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 bridge the opening fracture surfaces at the crack tip and the fracture phenomenon requires the tearing of rubber particles which absorb substantial level of energy thereby exhibiting increased toughness

A tear energy toughening model for the toughening of thermosets has also been proposed [17]. According to this model, the particles stretch across the crack opening behind the crack tip and hinder the advance of crack. According to this model, for a toughened thermoset, the energy absorbed in fracture is the sum of the energy required to fracture a material and to break the rubber particles. [17, 26]

Lately, it has been suggested [27, 28] that the major toughening mechanism is the plastic deformation of the matrix. Plastic deformation blunts the crack tip which reduces the local stress concentration and allows the material to support higher loads before failure occurs. Apart from the above, cavitation of the rubber particles and shear banding of the matrix are also major contributors to the increased 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. The cavity is stabilized by good adhesion, often due to chemical covalent bonding between the rubbery domains and the matrix resin; the cavities thus absorb the stresses on the matrix and increase the toughness of the thermosetting polymer. Plastic shear deformation bands are formed as a result of stress concentration in the matrix caused by the presence of rubbery particles. 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. Many thermosets have been toughened in this fashion [29,

30]. In 1980's, "rigid-rigid polymer alloy concept" was introduced, when substantial toughening was observed in epoxy 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 epoxy which later precipitate out as second phase particles. Polyether sulfone (PES)[29], polysulfone[31], 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. Epoxy polymers have also been toughened by the addition these fillers[32] 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[33] and later developed by Evan et.al. [34]. According to this model, the toughness improvement was dependent on the volume fraction and particle size of filler. The increase in fracture energy of a brittle material due to the addition of a brittle and second phase was explained by interaction between the propagating crack and the filler phase. When a crack begins to propagate through the resin, the crack front bows between the filler particles but remains pinned at the particles. In this way 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 [27, 35-37].

In the present study, silicone microspheres have been employed to improve the toughening of epoxy. Because of the incompatible nature of the silicone resin and organic matrix, most compositions necessitate introduction of a compatibiliser. Another alternative is the introduction of an additional layer of epoxy, i.e. development of core shell PDMS-Epoxy 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 with the general formula of $R_nSiX_mO_y$, where R is, usually Methyl or Phenyl, and X is a functional group H, OH, Cl or OR. These groups are further condensed in many applications, to give highly crosslinked, insoluble polysiloxane networks.

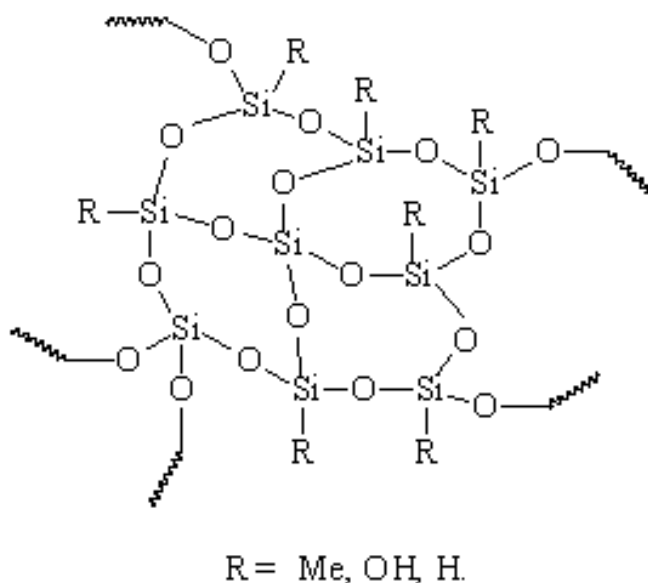


Figure 1.1: Cage like structure of silicone resin

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

- "M" stands for Me_3SiO ,
- "D" for Me_2SiO_2 ,
- "T" for MeSiO_3 and
- "Q" for SiO_4 .

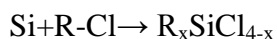
The most abundant silicone resins are built of D and T units (DT resins) or from M and Q units (MQ resins), however many other combinations (MDT, MTQ, QDT) are also used in industry.

Basically silicones occupy a hybrid position between inorganic and organic compounds, specifically between silicates and organic polymers. The siloxane link (Si-O-Si), also found in silicates, is responsible for the "inorganic" character. The organic properties arise from the direct link between silicon and carbon. Silicone resins are prepared by hydrolytic condensation of various silicone precursors.

1.4.1 Silicone resin synthesis

- *Muller-Rochow synthesis*

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



The composition and number of the structural units and the functional groups on the silicon atom determine the structure, processing, and complex properties of the silicone resins.

1.4.2 Properties of Silicone resin

The properties of the silicone resin are the important reason for its wide application and commercial success.

- Thermal stability

- Weathering resistance
- Maintaining elasticity at low temperatures
- Low surface tension
- Hydrophobicity
- Surface activity
- Release and lubricating properties

These properties make silicone resins and silicone combination resins widely applicable in areas such as impregnation of concrete and polymeric resins, high-temperature resistant coatings or weather resistant exterior coatings. These binders are used in the form of solutions, liquid resins and emulsions.

There have been attempts to blend silicone resins with epoxy to improve its toughenability. Curing of the thermoset in the presence of rubber leads to its precipitation, resulting in the formation of phase separated blends.^[21] However, blends with liquid rubber suffer from specific disadvantages including reduced elastic modulus, low glass transition temperatures and high water absorption

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 epoxy resin. A brief introduction of microspheres is presented in the following section.

1.5. Silicone microspheres

Microspheres are small spherical particles, with diameters in the micrometer range (typically 1 μm to 1000 μm (1 mm)). These can be prepared from various natural and synthetic materials. Glass microspheres, polymer microspheres and ceramic microspheres are commercially available.

Solid and hollow microspheres vary widely in density and, therefore, are used for different applications. Hollow microspheres are typically used as additives to lower

the density of a material. Solid microspheres have numerous applications depending on what material they are constructed of and what size they are.

Because of their size and shape, Microspheres offer a ball-bearing effect which will impart finished products with an elegant silky texture, increased payoff, and enhanced slip

Polyethylene, polystyrene, silicone and expandable microspheres are the most common types of polymer microspheres. Silicone microspheres are mainly used in biomedical application due to 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-Epoxy Core shell

To improve the compatibility of the silicone with the base epoxy resin, it was decided to introduce an additional layer of epoxy on the PDMS microspheres. The resultant microspheres were expected to possess a core shell morphology with an inner core of PDMS, coated with a shell of epoxy. This was achieved by suspension curing of the epoxy resin over the suspended elastomeric template of silicone (PDMS). The amount of epoxy resin was chosen, based on the required shell thickness (20 micron).A representative core shell morphology is presented in Figure

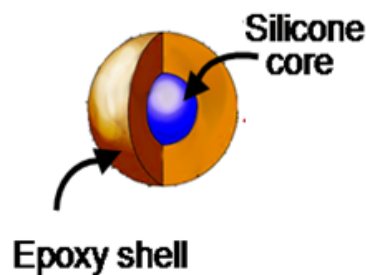


Figure 1.2: PDMS-Epoxy Core shell

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 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. The reaction mixture consists of two phases, a liquid matrix and monomer droplets. The monomer and initiator are insoluble in the liquid phase, so they form drops within the liquid matrix. A suspension agent is usually added to stabilize the monomer droplets and hinder monomer drops from coming together. The reaction mixture usually has a volume ratio of monomer to liquid phase of 0.1 to 0.5. The liquid phase acts as a heat transfer agent, enabling high rates of polymerization with little change in the temperature of the polymerizing solution. The reactions are usually done in a stirred tank reactor that continuously mixes the solution using turbulent pressure or viscous shear forces. The stirring action helps to keep the monomer droplets separated and creates a more uniform suspension, which leads to a more narrow size distribution of the final polymer beads. The polymerization is usually carried to completion. The kinetics of the polymerization within an individual bead is similar to that of typical radical polymerization.

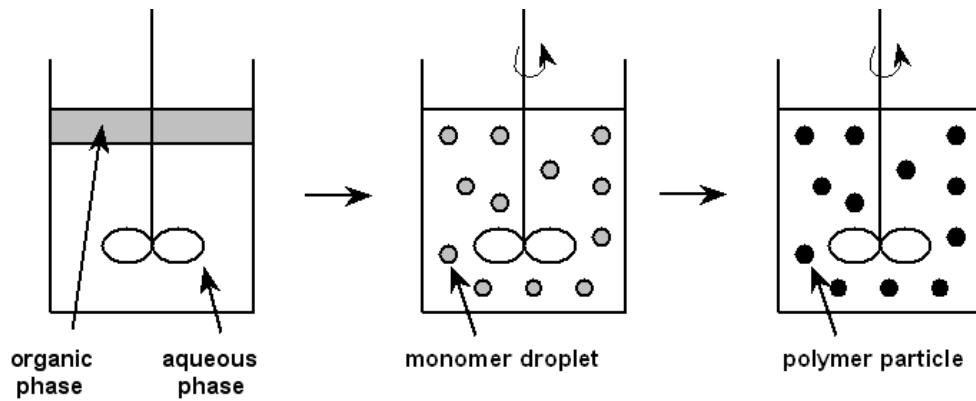


Figure1.3: Schematic representation of Suspension polymerization

1.7.2. Emulsion polymerization technique

Emulsion polymerization is a type of heterogeneous radical polymerization that usually starts with an emulsion incorporating water, monomer, and surfactant. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified with surfactants in a continuous phase of water. Water-soluble polymers, such as certain polyvinyl alcohols or hydroxyl ethyl celluloses, can be used to act as emulsifiers/stabilizers. Agitation and proper control on the emulsifiers / stabilizers 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. These latex particles are typically 100 nm in size, and are made of many individual polymer chains. The particles are stopped from coagulating with each other because each particle is surrounded by the surfactant, the charge on the surfactant repels other particles electrostatically.

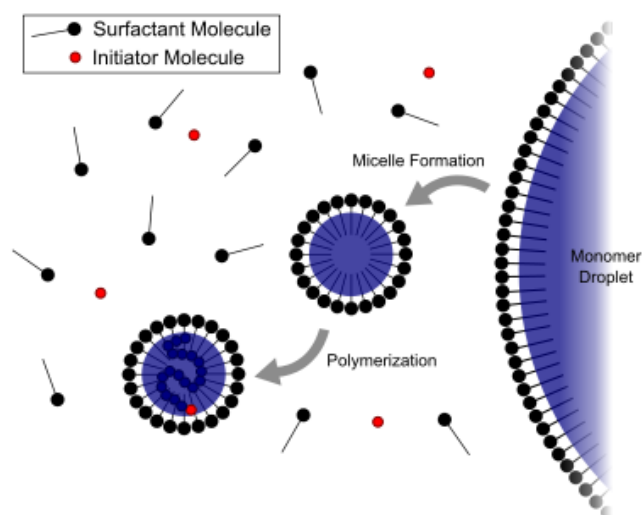


Figure 1.4: Micelle formation during emulsion polymerization

1.8. Project aims and objectives

This project deals with a novel approach to toughening of epoxy thermoset by the use of elastomeric microspheres, such as silicone microspheres and core shell silicone- epoxy microspheres. The effect that these microspheres have on the toughness of epoxy 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, thereby absorbing large amounts of energy. The additional layer of epoxy as a shell onto the core silicone microsphere helps to achieve better interfacial adhesion due to good compatibility between the 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. Unmodified cured epoxy 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/Epoxy microspheres.
- To prepare epoxy composites containing the developed microspheres.
- To investigate the effect of increasing loading of the fillers on the mechanical, thermal and structural properties of the composites.

CHAPTER 2

EXPERIMENTAL

2.1. Introduction

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

2.2. Materials

Silicone resin (Elastosil M4644) and the platinum based hardener was obtained from the Wacker, Germany. Epoxy resin (Ciba Geigy, Araldite CY 230; epoxy equivalent 200 eqg⁻¹) and hardener (HY 951; amine content 32 eqkg⁻¹) was used as received. PVA (Mol. wt. 14000, CDH) and chloroform (CDH) were used without any further purification. Distilled water was used throughout the course of study.

2.3. Preparation of core siloxane microspheres

The PDMS core was prepared using a batch suspension polymerization process. The vinyl terminated macromonomer was dissolved in chloroform in varying amounts (30-60% w/v) to which requisite amounts of platinum based hardener (10:1:: resin : hardener) was added 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 through which the feed was introduced with a hypodermic syringe. The reactor contained the suspending agent, PVA (1.5% w/v), which was maintained under continuous stirring (500-700 rpm) at 45°C. The polymerisation reaction was allowed

to continue for 8 h, after which the reaction mixture was cooled and the microspheres were filtered, washed with water and dried under vacuum at 80°C for 2 h. The extent of conversion was measured gravimetrically as the ratio of mass of microspheres to the amount of macromonomer used for its preparation. The schematic of formation of oil in water silicone droplets during suspension polymerization are shown below.

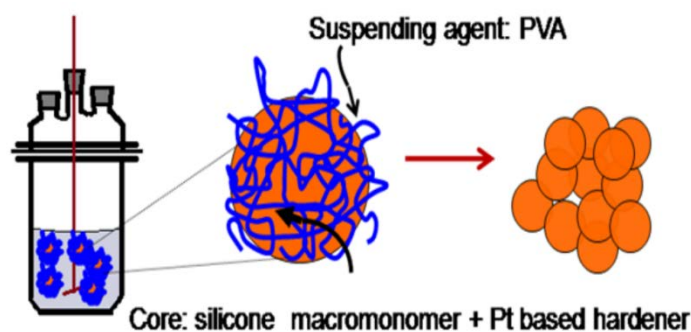


Figure 2.1: Formation of oil in water silicone droplets during suspension polymerization

2.4. Preparation of core-shell PDMS

The PDMS microspheres were coated with epoxy in a separate curing step. For this purpose, the PDMS microspheres (15g) were added to (7g) epoxy resin, and the mixture was ultrasonicated for 15-30 min, before addition of stoichiometric amount of hardener. Subsequently, 5 ml of chloroform was added, and the slurry was introduced into a reactor containing 1.5 L of PVA solution (1.5% w/v), maintained under stirring at 50 °C for 5 h to ensure complete curing of epoxy on the PDMS core. The schematic of PDMS templated epoxy curing process are shown below.

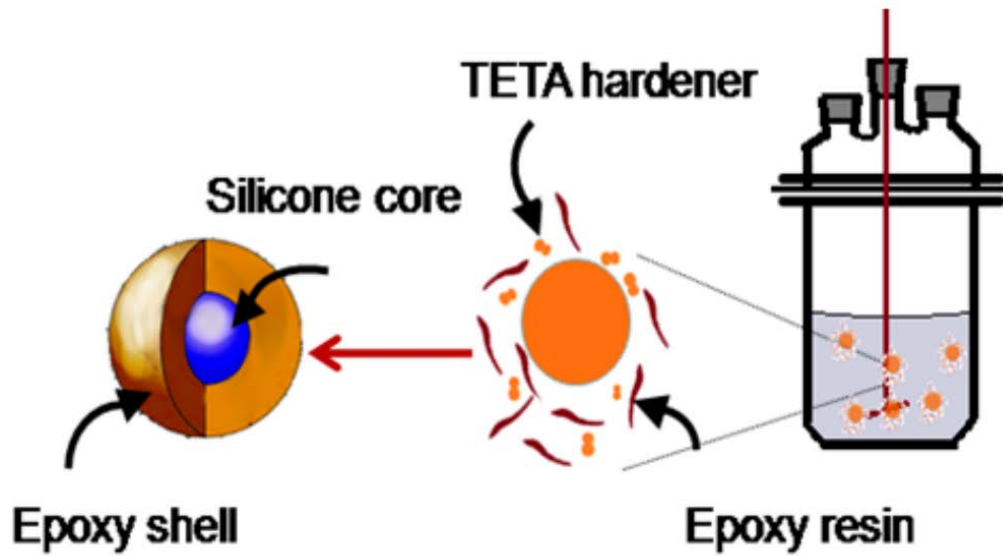


Figure 2.2: Schematic of PDMS templated epoxy curing process

2.5. Characterization

2.5.1. Particle size analysis

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

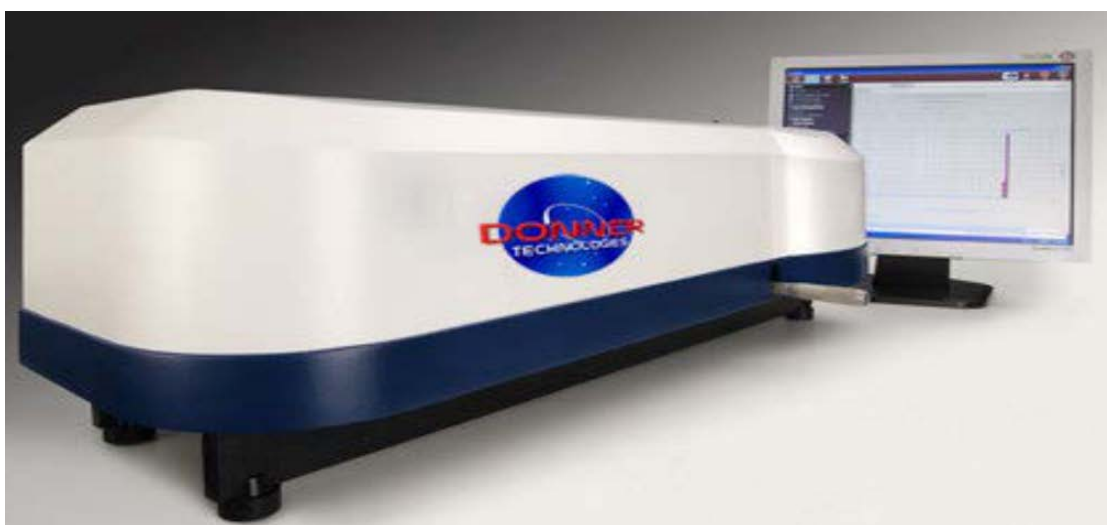


Figure2.3: Particle size analyzer

Principle

Laser particle size analyzer works according to the optic properties, particularly to laser such as monochromaticity, collimation, easily caused diffraction and scattering. In case beam illuminates the particles distributed in the liquid, the diffraction and scattering phenomenon take place. When the diffracted or scattered light passed through Fourier lens, a series of light rings emerge on the focal plane, radius of which are related to the size of the particles; the density of light is determined by number of particles. By circular array of photo detectors on focal plane, diffraction and scattering signals from the particles in different diameters are received. Then the signals are transferred to the computer through A/D conversion or other ways, being processed according to Fraunhofer diffraction or Mie scattering theory. The particle size distribution of the sample is thus obtained.

Working and instrumentation

- **The laser channel** uses the laser obstruction time (LOT) principle for the diameter of the particles in dynamic flow. As particles passes through the analyzer it temporarily blocks the rotating laser beam. 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. The obstruction time is not influenced by optical or physical properties. In other words, the particle size is independent of refractive index, absorption, surface texture, porosity, electrical conductivity or any other kind of the sample pre-knowledge.

- **The Video channel** analyzes the shape of particles in dynamic flow. This channel is equipped with a CCD microscope video camera. Illumination is provided by a

synchronized strobe light, and the acquired images are displayed and analyzed. By means of image analysis software, the images are automatically processed and analyzed, and a series of size and shape parameters are evaluated. In this way thousands of sampled images can be collected during a measurement cycle. All measurement results can be presented in multiple types of graphs and tables, and sample image can be stored for analysis at later time.

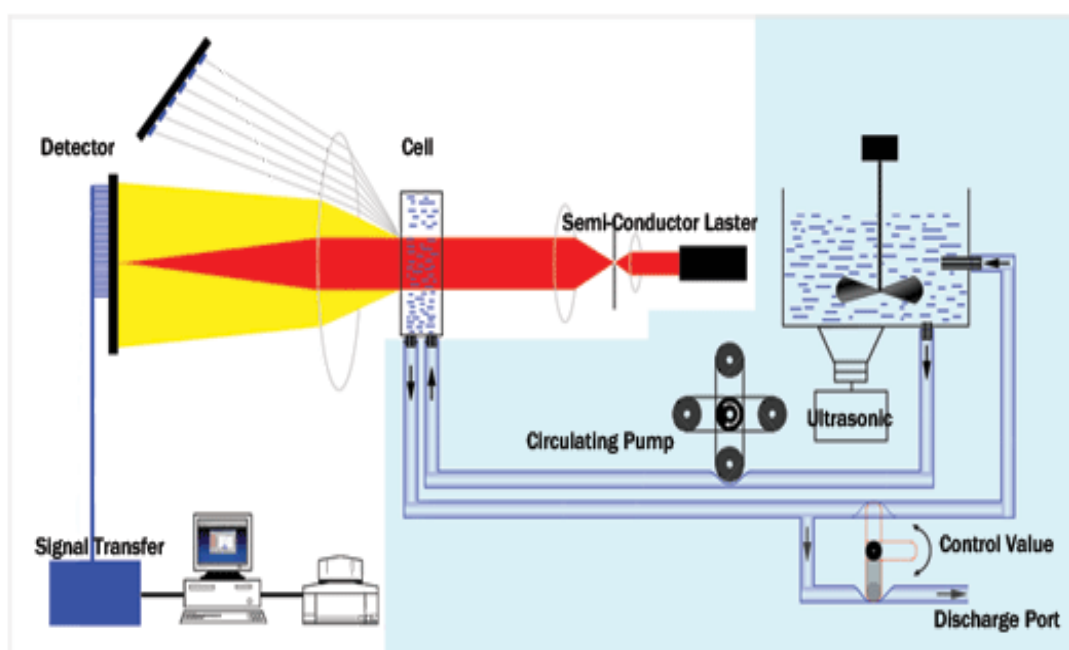


Figure 2.4: Schematic diagram of working of the particle size analyzer

2.5.2. Scanning electron microscopy

The surface morphology of samples was studied using a Scanning Electron Microscope (Zeiss EVO MA15) under an acceleration voltage of 20 kV. Samples were mounted on aluminium stubs and sputter-coated with gold and palladium (10 nm) using a sputter coater (Quorum-SC7620) operating at 10-12 mA for 120 s. The core shell structure of the epoxy coated PDMS microspheres was also confirmed

using EDX. For this purpose, a representative epoxy coated microsphere was cut with a sharp razor blade and carefully mounted on a stub and sputter coated with gold. The elemental composition in the core and shell region was determined using an energy dispersion analyser (EDS).

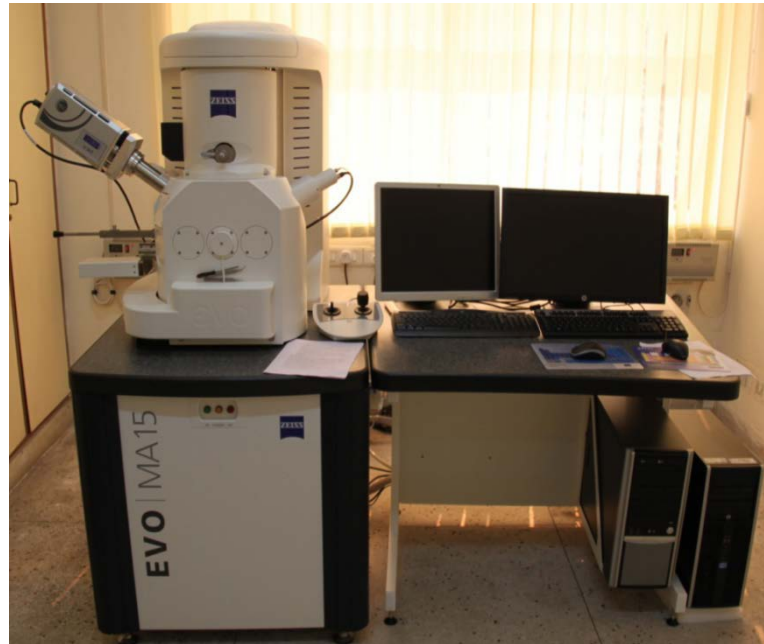


Figure 2.5: Scanning electron microscope

Principle:

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce 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 elemental analysis and continuum X-rays), visible light

(cathodoluminescence--CL), and heat. 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:

Essential components of all SEMs include the following:

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements:
 - Power Supply
 - Vacuum System
 - Cooling system
 - Vibration-free floor
 - Room free of ambient magnetic and electric fields

SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

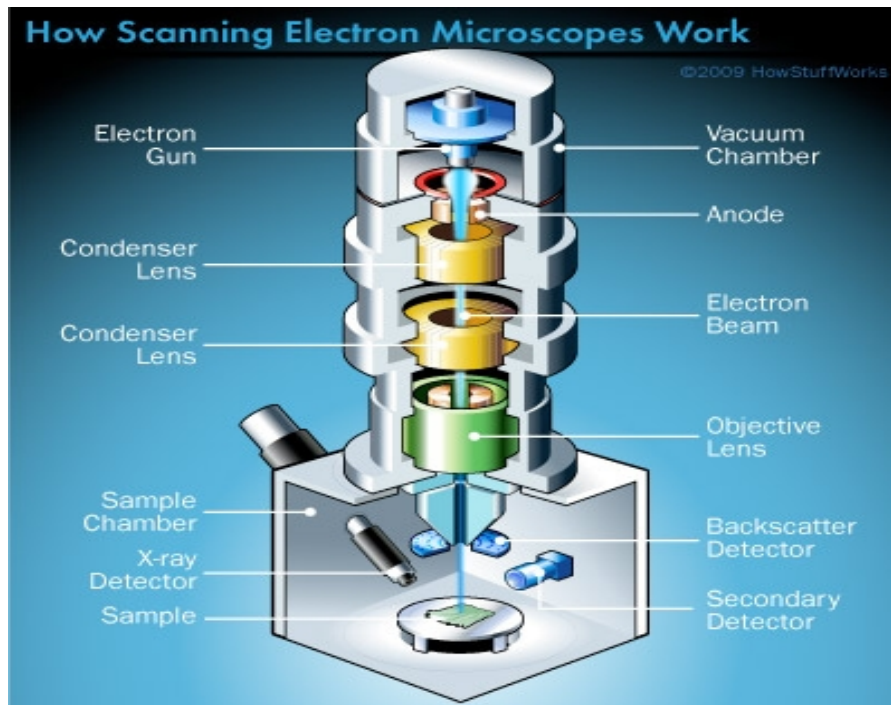


Figure 2.6: Schematic diagram of the working of a scanning electron microscope

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 operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample. An infrared beam is directed on to an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. It can be easier to think of this evanescent wave as a bubble of infrared that sits on the surface of the crystal. This evanescent wave

protrudes only a few microns ($0.5 \mu - 5 \mu$) beyond the crystal surface and into the sample. Consequently, there must be good contact between the sample and the crystal surface. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum.

2.5.4. Thermal Analysis

The thermal behaviour was investigated using Perkin Elmer Diamond STG-DTA under N_2 atmosphere (flow rate = 200 ml/min) in the temperature range 50-800 °C. A heating rate of 10 °C/min and sample mass of 5.0 ± 0.5 mg was used for each experiment.



Figure 2.8: Thermogravimetric analysis

Principal

Thermogravimetric analysis (TGA) is based on the measurement of mass loss of material as a function of temperature. In thermogravimetry a continuous graph of mass change against temperature is obtained when a substance is heated at a uniform rate or kept at constant temperature. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. A plot of mass change versus temperature (T) is referred to as the thermogravimetric curve (TG curve).

2.5.5. Mechanical Characterization

The mechanical properties of polymers are of great interest to scientists and relevant to industry. In order to fully understand the constitutive behaviour of these materials, high strain rate behaviour must be examined. The deformation properties of materials at high strain rates depend on atomic and molecular behaviour which may be very different from that found at low rates. The relationship between temperature and strain rate in both polymers and metals potentially gives better understanding of the high strain rate properties of these materials by relating them to quasi-static measurements. An understanding of when these relationships do and do not hold would be particularly useful for future research activities. Usually, the mechanical properties (strength and modulus) increases 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

2.5.5.1. Quasi static testing

In solid mechanics, quasi static loading refers to loading where inertial effects are negligible. In other words time and inertial mass are irrelevant. 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 sec^{-1} . Quasi static testing can be performed in either modes to evaluate the tensile, compression and flexural properties of the said material.



Figure 2.9: Universal Testing Machine (UTM)

Tensile Testing (ASTM D 638)

The determination of mechanical properties tensile strength, tensile modulus and strain-at-break were performed at ambient temperature as per ASTM method D 638 using an International equipment Universal Testing System (3369). Dumb bell shaped specimens were prepared for tensile testing by mixing required amounts of epoxy, hardener and the different modifiers. The dog-bone shaped specimens used in the tensile testing were 165 mm long, 3 mm thick and 13 mm wide along the centre of the casting for epoxy resin. The samples were subjected to a cross head speed of 50 mm/min during the tensile tests. At least three specimens were tested to obtain the effective average value of tensile properties

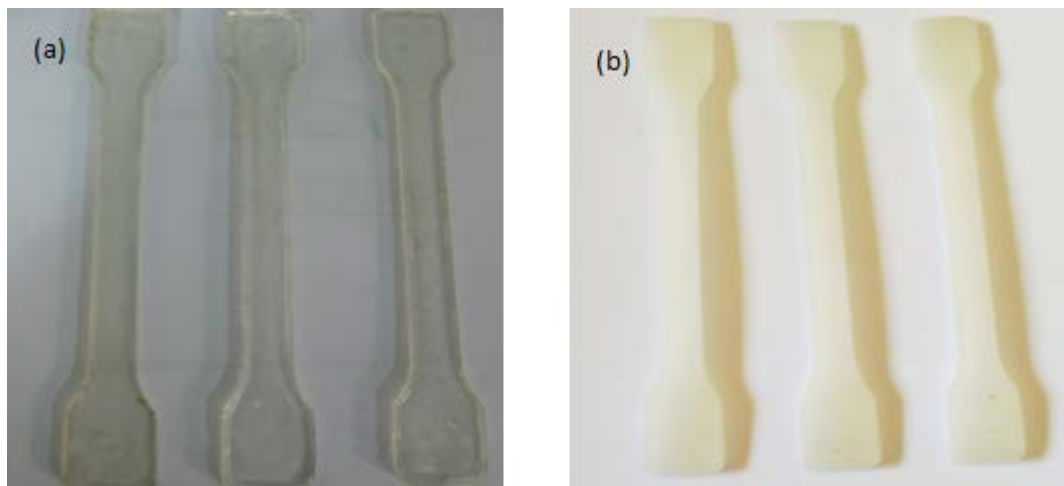


Figure 2.10: Photographs of samples a) neat Epoxy b) Microspheres reinforced epoxy

Flexural testing (ASTM D 790)

Notched flexural testing of the samples was performed under three point single edge notch bending mode. For this purpose, specimens of requisite dimensions (127 mm length x 12.5 mm width x 3.5 mm thickness and 3 mm notch) were prepared and

subjected to a deformation rate of 2 mm/min while maintaining 60 mm span length. The data obtained was analysed to determine the mode I fracture toughness (K_{IC}) of the samples as per the following equation: [39]

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

Where, P, L and B refer to the load at break, span length and sample thickness respectively. The geometry factor, $Y\left(\frac{a}{w}\right)$, is calculated as per the formula below,

where a is the notch length and w is the sample width.

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

2.5.5.2. 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 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.

Charpy Impact testing (ASTM D 4812)

The Charpy 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.). The energy absorbed is measured. This absorbed energy is a measure of the impact strength of material. 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 subjected to a deformation.



Figure 2.11: Impact testing machine

2.5.6. Swelling studies

Swelling index of the cross linked microspheres were determined by placing accurately weighed samples (500 mg, in triplicate) in different mediums such as distilled water, methanol, acetone, xylene, toluene, chloroform, ammonia, tetrahydrofuran (THF), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and hexane for extended time period (72 h), after which they were removed, tapped dry and re-weighed. The swelling index was quantified as the ratio of mass of solvent imbibed to the initial mass of microspheres used for the experiment.

2.6. Preparation of epoxy composites

Toughened epoxy composites containing varying loadings of both coated and uncoated microspheres (3-10 %) w/w were prepared by adding requisite amounts into the epoxy resin followed by ultrasonication of the resulting mixture for 30 min at 33 kHz. For this purpose, the microspheres were sieved through a 60/80 mesh and the particles between the particle size 250 to 177 μ were collected for the use as filler. Triethylenetetraamine hardener was subsequently added to the mixture (13 phr), to achieve an amine: epoxide stoichiometry of 1:1 and ultrasonicated for another 15 minutes to remove any entrapped air bubbles. The suspensions were degassed under vacuum and transferred to greased cylindrical stainless steel molds, where the curing reaction was allowed to proceed for 24 h at 30°C. Neat epoxy specimens were also prepared in a similar manner and the details of all the compositions prepared are listed in Table 1. The samples have been designated as EP followed by its concentration and by the type of microsphere used for its preparation, i.e. 'R' denotes uncoated PDMS microsphere and 'CSR' denotes epoxy coated core shell microspheres with PDMS core.

Table 1: Sample designation and compositional details

Sample	Amount		
Designation	Epoxy resin (g)	Hardener (g)	Microsphere (g)
EP	100	13	-
EP3x	100	13	3.3
EP5x	100	13	5.6
EP7x	100	13	7.9
EP10x	100	13	11.3

x denotes the type of filler (R: PDMS, CSR: core shell PDMS)

CHAPTER 3

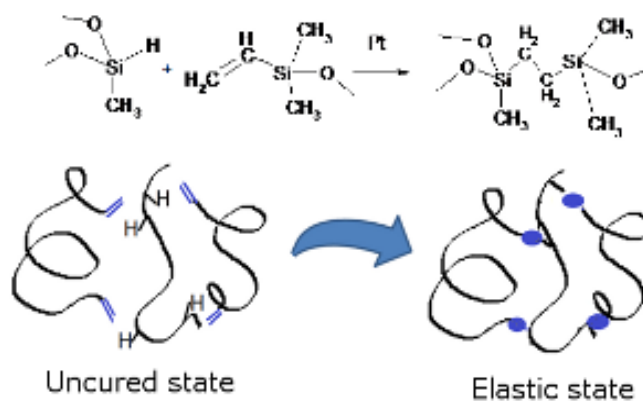
RESULTS AND DISCUSSION

This project deals with an approach to improve the energy absorption characteristics of epoxy thermosets. Several methods have been employed for toughening epoxy 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- epoxy shell microspheres by suspension polymerization process, with an aim to improve the compatibility between the preformed elastomer and the epoxy resin. The effect of introduction of these rubbers on mechanical and thermal properties has been evaluated.

3.1. Suspension curing of siloxane

Suspension polymerization is one of the most common techniques 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. In the present study, the vinyl terminated methyl hydrosiloxane-dimethylsiloxane copolymer was cured at 45°C in the presence of a platinum based hydrosilylation catalyst[40] as per reaction scheme 3. 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 3: Platinum catalysed hydrosilylation of silicone.

3.2. Effect of concentration on particle size

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

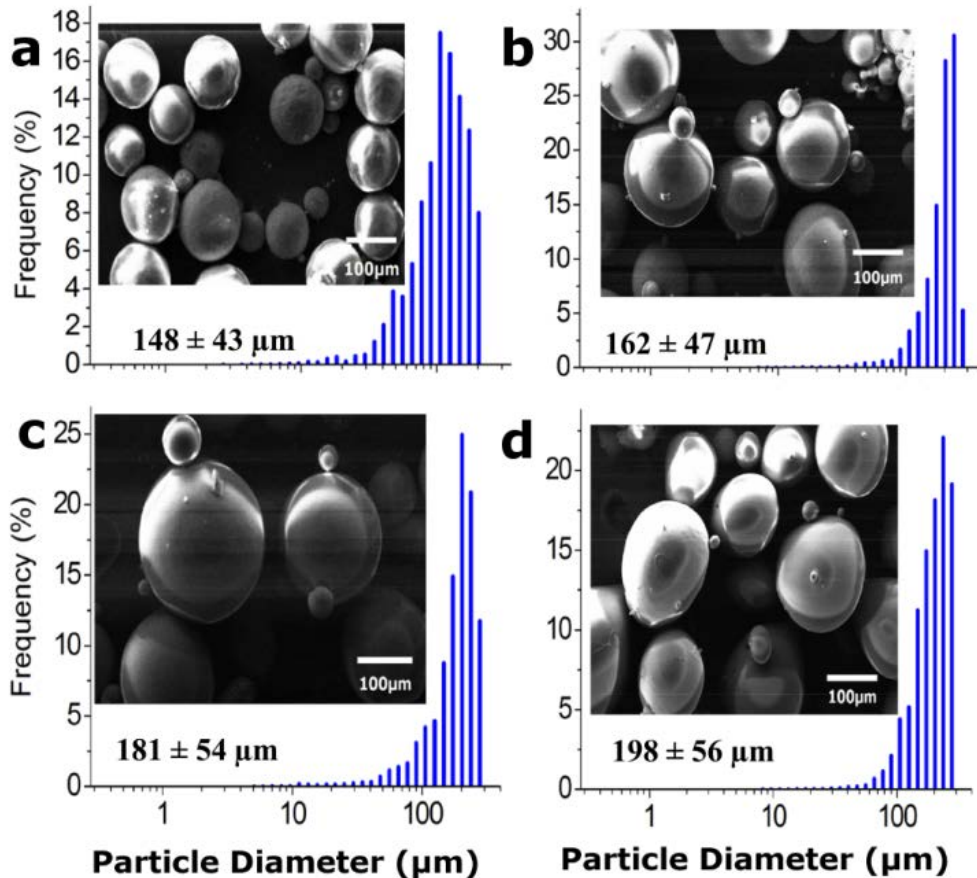


Figure 3.1: Effect of feed concentration on the particle size distribution and surface morphology of PDMS microspheres (stirring speed 600 rpm). a) 30% b) 40% c) 50%
d) 60%

The effect of varying the stirring speed on the particle size distribution of the microsphere was also studied and these results are presented in Figure 3.2, (feed concentration 60 % w/v). It can be seen that with increase in the stirring speed, the particle size distribution shifts towards lower size, which could be attributed to the shearing of the large oily droplets into smaller microspheres, which stabilise in the presence of surfactant even at high stirring speed.

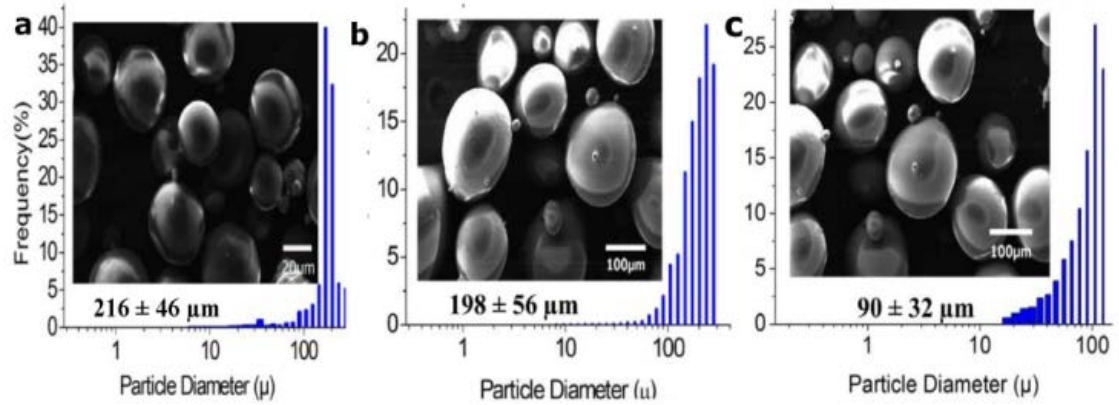


Figure 3.2: Effect of stirring speed on the particle size distribution and surface morphology of PDMS microspheres. a) 500 rpm b) 600 rpm c) 700 rpm

3.3. Effect of coating on microsphere dimensions and morphology

With an aim to improve the compatibility of the elastomeric microspheres with the thermosetting resin, the microspheres were coated with a layer of cycloaliphatic epoxy separately. As expected, coating of PDMS microspheres led to an increase in the particle dimensions, which was determined by particle size analysis. As a representative case, the size distribution of core shell PDMS -epoxy microspheres prepared using 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 μ . Interestingly, in comparison to that of neat PDMS, the surface of the coated microspheres was found to be rather rough.

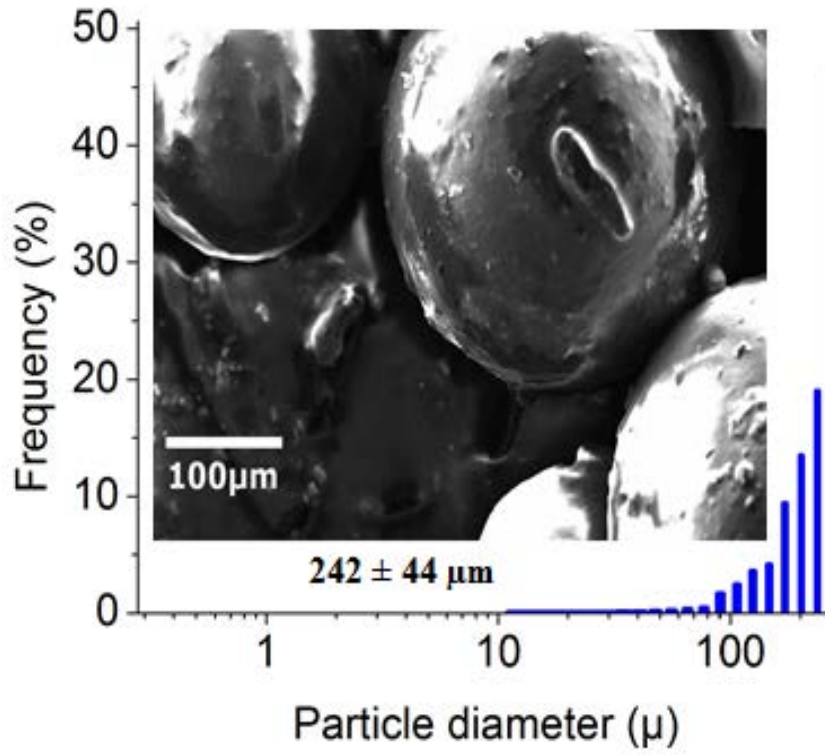


Figure 3.3: Particle size distribution and surface morphology of coated microspheres

3.4. Elemental analysis

The elemental composition of the coated and uncoated PDMS microspheres was determined by EDX. The values were averaged over a specific square area within a microsphere (Figure 3.4). As can be seen, the amount of silicon present in the shell is practically negligible, which confirms the coating of epoxy on the PDMS core.

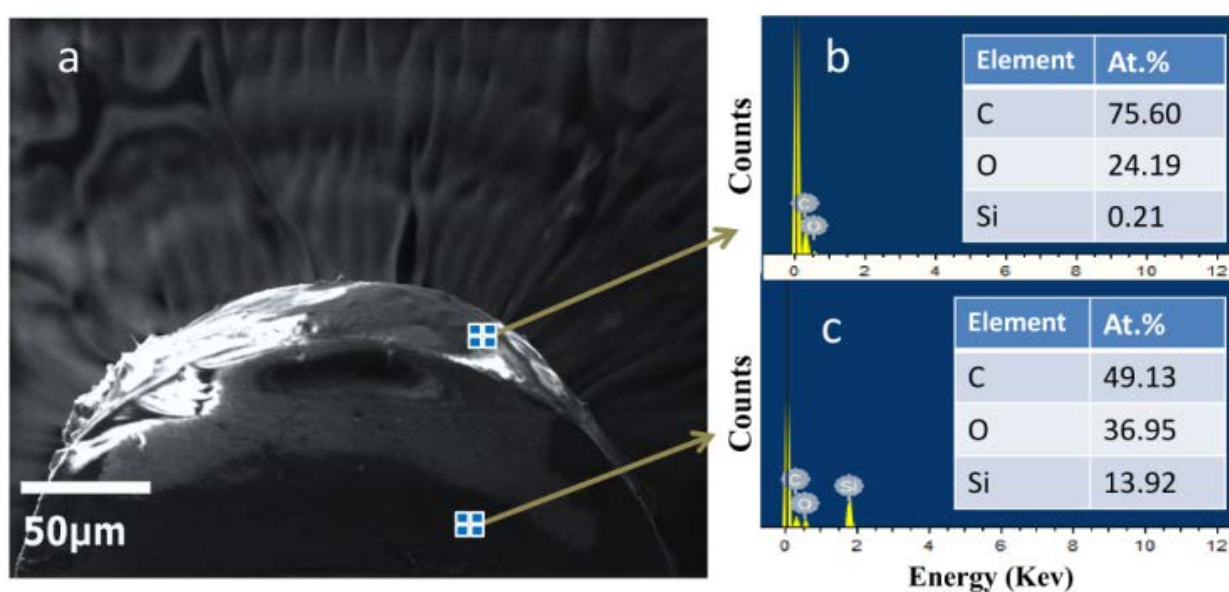


Figure 3.4: Cut cross section of single coated microspheres (a) SEM image, and EDX analysis (b) shell (c) core.

3.5. Structural properties

The FTIR of the PDMS, both before and after epoxy coating is presented in Figure 3.5. In the FTIR spectra of PDMS, characteristic absorption peaks at 802 and 1258 cm^{-1} were observed, which could be attributed to the $(\text{CH}_3)_2\text{SiO}$ group vibration in the polymer.[41] Additionally a broad absorption at 1000-1130 cm^{-1} was also observed, which can be attributed to the Si-O-Si vibration. Epoxy coated microspheres, exhibited additional absorption bands at 1100 cm^{-1} due to the asymmetrical stretching vibration of polyether.[42] Appearance of additional absorption in the region 1250–1360 cm^{-1} due to ν_s (C-N) and 1580–1650 cm^{-1} due to ν_s (N-H) also confirms the coating of epoxy on the PDMS surface.

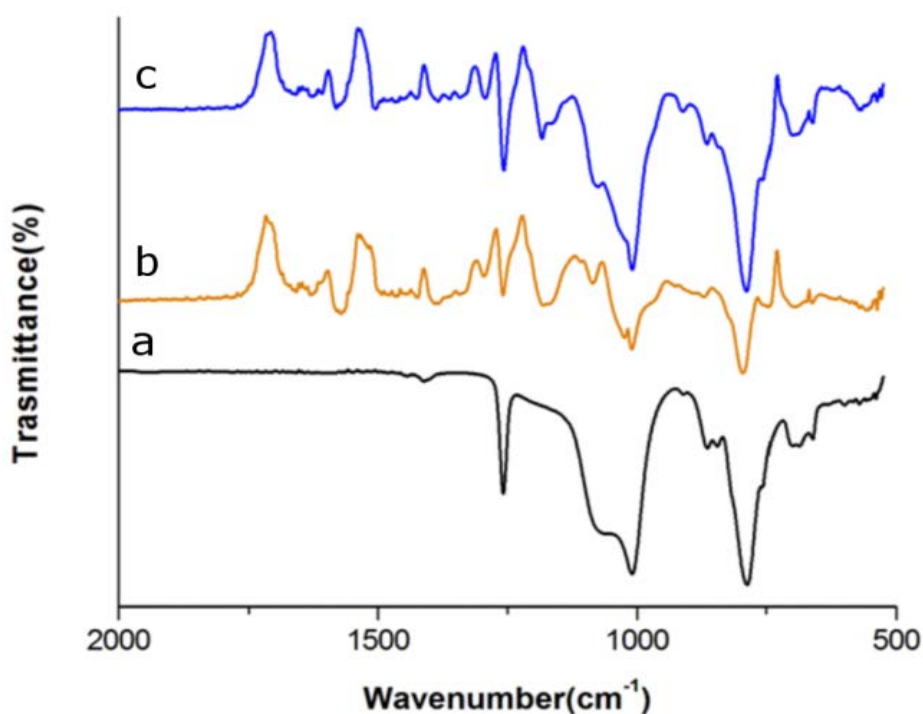


Figure 3.5: FTIR spectra of a) PDMS, b) Neat Epoxy c) CSR

3.6. Thermal degradation

PDMS exhibits excellent thermal stability and the same is evident from the TG-DTG traces, which are presented in Figure 3.6. The elastomer exhibits a single step decomposition initiating at ~ 400 °C leaving behind a residual mass of $\sim 65\%$, which is consistent with the results reported previously.[43, 44] Although the weakest bond in PDMS is the C–Si (326 kJ mol^{-1}), the presence of cyclic oligomers in the decomposition product suggests that the Si–O bond (451 kJ mol^{-1}) cleaves instead which indicate that the depolymerization process is governed mainly by the molecular structure and kinetic considerations, and not by bond energies. [45] Coating the PDMS microspheres with epoxy led to a change in the thermal degradation behaviour and a two step degradation was observed. The first pyrolytic degradation occurs due to the cleavage of C–C, C–O and C–N bonds at much lower temperatures ($T_{\text{onset}} \sim 200$ °C) and the second step results from the degradation of the core silicone.

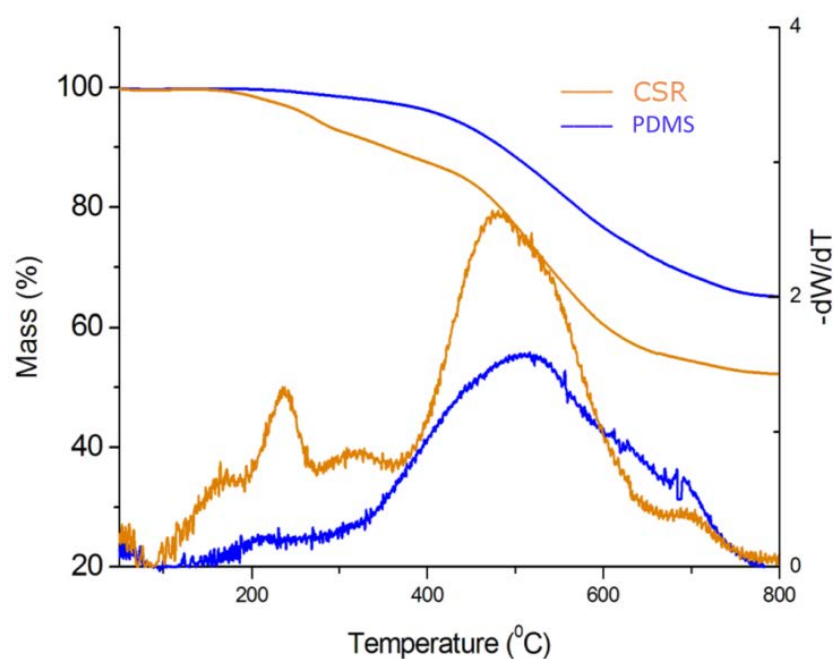


Figure 3.6: TG-DTG traces of a) PDMS b) epoxy coated microspheres.

3.7. Swelling index

The effect of coating on the extent of swelling was measured by gravimetric studies which reveal that PDMS microspheres were chemically inert, with the mass loss being practically negligible on being placed in common solvents. Likewise the core shell PDMS epoxy microspheres did not swell in any of the solvents but as expected the epoxy layer turned brittle on extended exposure to a few solvents, namely methanol, chloroform and toluene and a mass loss of 15 ± 4 % was observed.[46]

3.8. Epoxy-PDMS composites

Composites of epoxy containing both PDMS microsphere and core-shell microspheres were prepared by dispersing them within the resin by ultrasonication followed by curing with the amine hardener in requisite ratio. The cured polymer was evaluated for its mechanical and thermal properties.

3.8.1. Mechanical properties

3.8.1.1. Impact strength

The introduction of elastomeric microspheres led to a remarkable improvement in the impact strength of epoxy, as is evident from figure 3.7. The Charpy impact strength increased from 22.5 Jm^{-1} (neat Epoxy) to 55.8 Jm^{-1} (~148 % increase) on addition of 5 % w/w CSR. Similar increase in the toughness at such low loadings have been reported earlier. [47] In comparison, the improvement in impact strength was less pronounced when uncoated PDMS was used as the filler.

There are two major criteria for the elastomeric microspheres to meet in order to exhibit their full potential as impact modifiers for epoxy. 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 epoxy shell of the CSR strongly interacts with the epoxy during the curing process, which leads to its better dispersion as compared to its uncoated analogue. However, with increased loadings, the impact strength decreased, which can be attributed to the agglomeration of these microspheres.

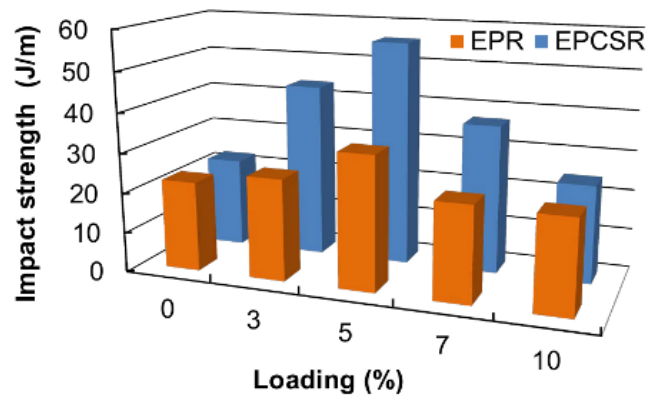


Figure3.7: Effect of elastomeric microspheres on impact strength of epoxy.

The morphology of the fractured surface was studied by SEM imaging and the results are presented in figure3.8. As can be seen, the fractured surface of epoxy is smooth and featureless and shows no sign of plastic deformation, which is typical of a brittle thermoset polymer.[48]

In comparison, the surface of the fractured composite is rather rough. [33, 49, 50] 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 in the surface of fractured composites containing CSR. The presence of

silicone rubber within the broken microspheres presents a direct evidence of improved adhesion between the elastomeric phase and the epoxy matrix.

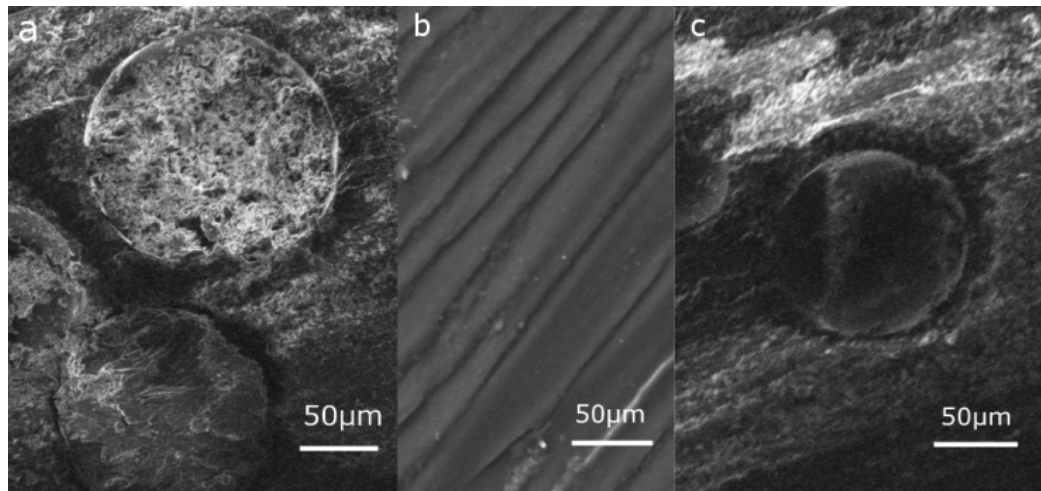


Figure 3.8: SEM image of the fractured surface of epoxy composite a) EP5CSR b) Neat Epoxy c)EP5R

Although the mechanism behind epoxy 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, 48, 51, 52] On being subjected to a dynamic load, the rubber particles tend to cavitate because of the tri-axial tension around the crack tip, which in turn relieves the in-plane strain ahead of the crack thus minimizing crack propagation. Moreover, these small and evenly dispersed microspheres also tend to act as crack terminators.

3.8.1.2. Quasi-static testing

Figure 3.9 presents the variation in mechanical properties of the epoxy composites containing both neat PDMS as well as core shell PDMS-epoxy microspheres. The introduction of elastomeric microspheres led to a decrease in the tensile strength and modulus, the extent of which was found to be proportional to the amount 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. [53] However, as expected on addition of these elastomeric microspheres a slight increase in the tensile strain was observed.

It has been reported that in comparison to acrylate based elastomer, the loss in mechanical strength and modulus is less pronounced when silicones are employed 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 epoxy 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.

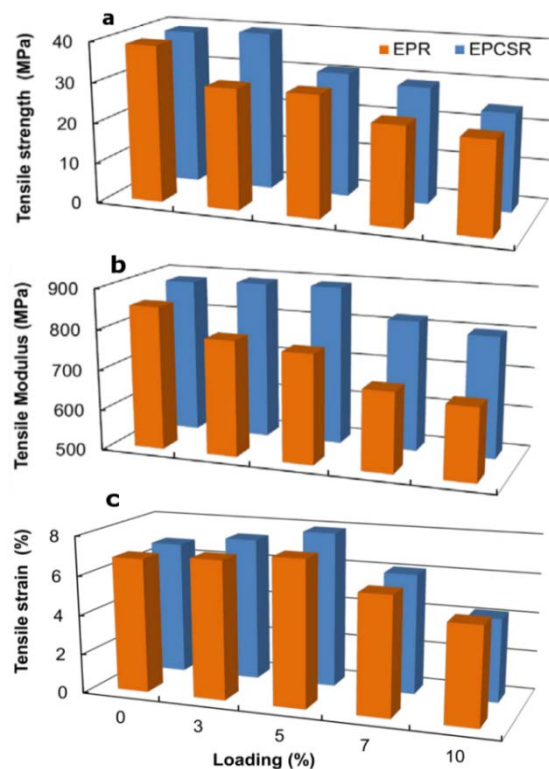


Figure 3.9: Effect of microsphere loading on mechanical properties of epoxy (tensile mode) a) Tensile strength b) Tensile strain c) Tensile modulus

3.8.1.3. Flexural strength

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 3.10. As expected, the introduction of elastomeric microspheres within the epoxy matrix led to an increased flexural strain, which can be attributed to the high extensibility of the rubbery domain. More importantly, the core shell PDMS-epoxy could be flexed to a higher extent, which in turn reflected in larger values of fracture toughness (K_{IC}). The introduction of notch led to a lowering in the flexural strength of specimens, which can be attributed to the stress concentration around the notch, which in turn leads to local yielding and initiation of cracks. A comparison of the fracture toughness (K_{IC}) as a function of composition type is presented in Figure 3.10. The Mode I fracture toughness of epoxy increased by ~30% in blends containing CSR, which is indicative of its potential towards improving the notch sensitivity of epoxy.

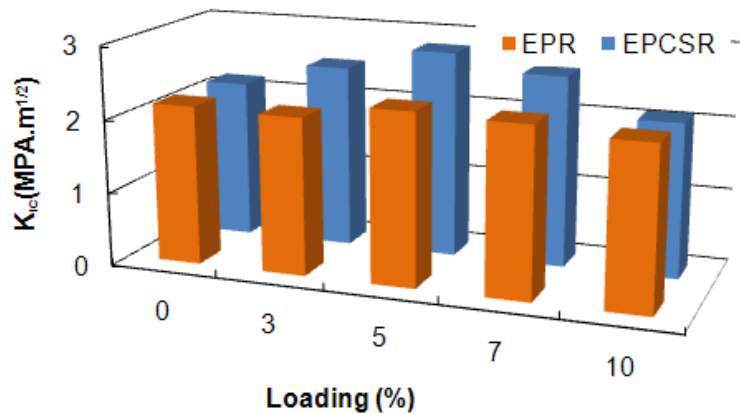


Figure 3.10: Effect of elastomeric microsphere loading on the fracture toughness (K_{IC}) of epoxy

3.8.2. Thermal characterization

The TG trace of epoxy and representative composites with PDMS and core shell PDMS-epoxy are presented in Figure 3.11. It can be seen that the introduction of elastomeric fillers do not affect the thermal properties of the base resin and all the compositions can be used in service till 250 °C, irrespective of the type of filler employed. The thermal decomposition of cured epoxy reportedly proceeds in two or more steps, depending on the type of resin employed. The first step is associated with evolution of water, which takes place at ~250°C. This is followed by the pyrolytic decomposition of the main chain at ~350 °C, which leads to the formation of condensables like acetone, carbon dioxide, hydrogen cyanide, aliphatic hydrocarbons etc. [54]

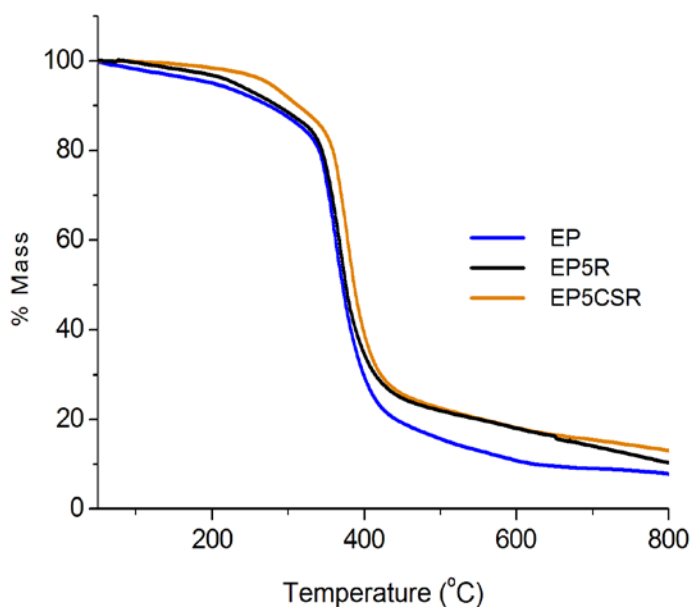


Figure 3.11: Thermogravimetric traces for neat epoxy and its composites containing PDMS and core-shell PDMS Epoxy (5% w/w)

CHAPTER 4

Summary and conclusion

Core-shell PDMS epoxy microspheres were prepared for use as impact modifier for thermosetting epoxy resin. The core elastomeric beads of PDMS microspheres were prepared by suspension polymerization process involving the addition reaction of silicone macromonomer in the presence of a platinum based hydrosilylation catalyst. The effect of operating parameters like stirring speed and feed concentration on the particle size distribution of the resultant microspheres was studied to monitored at optimum conditions. The microspheres were subsequently coated with an epoxy layer in a separate step to prepare core shell rubbers, in order to improve its compatibility with the epoxy thermoset. Both uncoated as well as epoxy coated PDMS microspheres were dispersed in the epoxy matrix to prepare toughened composites (3-10% w/w). The effect of addition of these fillers on mechanical properties (both quasi static and dynamic) was studied. The presence of the superficial epoxy coating on the elastomeric core seen to play important role in dispersion of the microspheres, which is evident from the mechanical property analysis. The investigated charpy impact strength increased by ~148 % on addition of 5 % core shell PDMS-epoxy. The thermal properties seem to be unaffected on addition of these fillers.

RECOMMENDATIONS FOR FUTURE WORK

The results obtained so far indicate that significant improvement in the tougheneability of epoxy 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.

- A detailed investigation of the dynamic behaviour of epoxy 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.

APPENDIX 2.1

2.1.1. DETERMINATION OF EPOXY EQUIVALENT

For the purpose of quantification of epoxy equivalent, a known amount of epoxy resin (~ 0.5 g) was refluxed with 25 ml of pyridine hydrochloride solution (6.25 ml of conc. HCl (12 M) in 250 mL freshly distilled pyridine) for a period of 20 min, which led to the formation of a transparent solution. Post-cooling, the contents were titrated against previously standardized potassium hydroxide solution (0.2 M) using phenolphthalein as an indicator. The end point was determined by the appearance of pink colour. The reading was noted as T2. A blank experiment was performed first in the absence of epoxy resin (recorded as T1) and the difference between the two sets (i.e., T1-T2) was used to quantify the epoxy content as per the following formula

The epoxy equivalent was calculated from (T1-T2) keeping in view that-

1 ml of 0.2 moles per litre potassium hydroxide = 0.0086 grams epoxide group

Therefore, epoxy equivalent = grams of polymer requiring 5000 ml of 0.2 moles per litre.

The epoxy equivalent was calculated to be 200 g/eq

2.1.2. DETERMINATION OF TOTAL AMINE CONTENT

The primary and secondary amine content (eq/g) was determined by pH metric titration method. A pre-weighed amount of AFAFC (0.3g) was dissolved in 1:1 water-isopropanol mixture (30 mL) and was subsequently titrated against 1.1 N

hydrochloric acid. The pH of the medium was recorded over the entire period, which was used to determine the amine content as per the following formula.

The plot of pH against volume of acid was used to calculate the amount of amine content. The total moles of amine per gram were determined using the following formula:

$$\text{moles of amine/g} = \frac{\text{volume of HCl (ml)} \times \text{Normality}}{\text{Amount of sample (g)} \times 1000}$$

The amine content is usually quantified by any of the following:

Amine Hydrogen Equivalent Weight (AHEW g/eq): This is more commonly referred to as equivalent weight per active Hydrogen, and is defined as the amount (g) of hardener containing one equivalent of N-H groups. This is calculated as Mw of the hardener divided by the number of active hydrogen per molecule

Parts per Hundred Resin (phr): It is defined as the grams of hardener needed per hundred grams of epoxy resin

Conversion: $\text{phr} = (\text{AHEW} * 100) / \text{EEW}$

Amine Value (Aminzahl): It is also sometimes called amine-index and is defined as milligrams of KOH equivalent to one gram of hardener.

Conversion: NO CORRELATION WITH AHEW

Amine content (Aminwert): It is given by equivalents of N-H per kg of hardener

Conversion: $\text{Amine content} = 1000 / \text{AHEW}$

1. Amount of hardener (HY 951) used

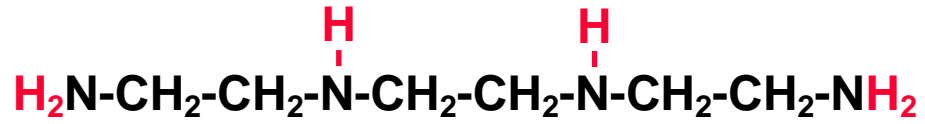


Fig: Hardener TETA

Molecular weight of the hardener = 146

No of active hydrogen per molecule = 6

Therefore, amine hydrogen equivalent weight (AHEW) = $146/6 = 24$ g/eq

Epoxy equivalent weight (EEW) = 200 g/eq

$$phr = \frac{AHEW}{EEW} \times 100$$

$$phr = (24 \times 100) / 200 = 12$$

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