CHAPTER 2
LITERATURE REVIEW

This chapter deals with the literature study on polymer composites. Out of two types of polymers (thermoset and thermoplastic), study is concentrated on thermosetting polymers (polyurethane elastomer and its composites) with respect to synthesis, and effect of reinforcement on polyurethane mechanical properties, and improvements in its performance have been reviewed.

2.1 POLYMER COMPOSITES

Polymers and their composites are emerging as viable alternative products to metal based ones in many common and advanced engineering applications. Ease of fabrication, availability of a good choice of materials from both thermoplastic and thermoset varieties and their economic viability have made the advent of these newer materials for industries ranging from automobile to sports goods [10].

Polymer composites are increasingly gaining importance as substitute materials for metals in applications within the aerospace, automotive, marine, and electronic industries. Their lightweight and superior mechanical properties make them ideally suited for transportation and other applications.

Polymer matrix composite materials offer many superior properties compared to with conventional materials, among them high strength to weight ratio, superior
corrosion resistance and the ability to tailor the material system to a particular requirement [11].

Composites have been mainly used for savings in secondary structures. With several advances made in understanding the behaviour of composite materials, many fibre reinforced polymer composite materials are finding increasing use as primary load bearing structures and in a wide range of high technology engineering applications. The composites have the ability to tailor design, in addition to high stiffness-to-weight ratio, fatigue resistance, corrosion resistance, and low cost when compared with conventional metals. The main drawback of composite systems when compared to metallic systems is their inability to resist defect initiation and propagation [12].

Fibrous composite materials typically have two or more distinct phases, which include high strength/stiffness reinforcing fibres and the encapsulating matrix material. Fibres can be either discontinuous (chopped) or continuous. Polymer matrices typically fall into two categories: thermoplastic and thermosetting polymers. Thermoplastic polymers are distinguished by their ability to be reshaped after the application of heat (above the glass transition temperature of the amorphous phase or the melting temperature of the crystalline phase). This cycle can be carried out repeatedly. Thermosetting polymers, on the other hand, undergo chemical reactions during curing which crosslink the polymer molecules. Once cross-linked, thermosets become permanently hard and undergo chemical decomposition with the application of excess heat. Thermosetting polymers typically have greater abrasion resistance and dimensional stability compared to thermoplastic polymers, which have better mechanical properties.
The use of fibre reinforced composite materials as an alternative to traditional metallic materials is becoming widespread. The main technological advantages of these materials are low weight, high specific strength and stiffness, environmental resistance and long life and energy absorption, indefinite shelf life and possibility of recycling. Compared to metals, composite parts can be easily made with relatively low tooling cost. In recent years, the usage of fibres used as reinforcement to improve the mechanical properties gained interest among researchers throughout the world. Electrical or E-glass is the most commonly used and most economical glass fibre when compared to structural or S-type glass [13].

Polymer composites with conducting carbon black, which may serve as polymer conductors or semi-conductors or the media for heat transferring, have found wide applications in electric and electronics industry. The advantage of conductive polymeric composites is their plastic nature, which makes them easy to prepare various products by using conventional processing techniques and there by reducing the manufacturing costs. The products generally are able to combine high electric conductivity with the favourable properties of polymer materials. A series of segmented polyurethanes with shape memory properties have been reported [14-18].
Polyurethanes have the advantages of low viscosity, excellent bonding with the matrix material without special sizing of the fibres, relatively low price and fast reaction time. The polyurethanes are an important and very versatile class of polymer materials with desirable properties, such as high abrasion resistance; tear strength, excellent shock absorption, flexibility and elasticity [19-21].

PU elastomers are a family of segmented polymers with soft segments derived from polyols and hard segments from isocyanates and chain extenders [22-23].

PU elastomers represent one of the most attractive elastomers because they have the advantages such as the best abrasion resistance, outstanding oil resistance, excellent low-temperature flexibility and extraordinary processibility. They also exhibit the widest variety of hardness and elastic moduli that just fill in the gap between plastics and rubbers. In other words, they can be tailor made as the materials with characteristics of either high modulus or good elasticity.

PU elastomers, however, have some disadvantages such as low resistance to moisture and hydrolysis, low resistance to polar solvents, and poor thermal stability. Generally, the acceptable thermal durability for PU ranges from 80 to 90° C, and the thermal degradation of PU occurs at 200° C [24].

These materials are used in corrosion-resistant composites, sporting goods, electronic and electrical engineering, chemical engineering, architecture, transportation, agriculture, aircraft and aerospace [25-28].
Polyurethane is an important type of polymeric material, widely used in performance materials such as adhesives, sealants, cast elastomers and coatings. Their properties depend greatly on the reactivity of hard and soft segments. The curing reaction kinetics of PU has been extensively studied and the results showed that the reaction of isocyanate with small molecular alcohol follows a second-order mechanism, but a small deviation at high temperature sometimes occurs [29].

2.3 SYNTHESIS OF POLYURETHANE

Polyurethanes can be prepared by a variety of methods. There are advantages and disadvantages for each method. The one-time polymerization result in a more random block polymer and the prepolymer method is a two-step process, which gives less random and more block polymers. This type of polyurethane consists of alternating segments of hard and soft blocks. The hard segments are formed by extension of an aromatic diisocyanate and the soft segments are polyethers or polyesters. The typical polyurethane is extensively hydrogen bonded, the donor being the NH group of the urethane linkage. The hydrogen bond acceptor may be either the hard or the soft segment.

Polyurethanes are usually produced by the reaction of a polyisocyanate with a polyl or other reactants containing groups reactive with isocyanate. The hydroxyl group component present in the polyurethane is usually used as a reactive material with polyisocyanate; it also has a wide range of molecular weight, in its types (polyether and polyester). The polyisocyanate also can have variable in its structure like aromatic, aliphatic and polycyclic. The physical properties of polyurethanes are dependent on polyols and isocyanates used. Similarly, the physical properties are also variable and the products derived can
have wide range of applications such as plastics, fibres, elastomers, films and surface coatings [30-32].

Polyurethanes prepared from polyol, diisocyanate, and curing agents are used commercially as coatings, adhesives, foams, castable elastomers and millable elastomers. Properties of polyurethanes can be varied a wide range depending on the chemical structures and the molecular weights of the soft segments. Physical and morphological properties of the polyurethane elastomers have been reviewed [33-36].

Pultrusion is an automatic and continuous process for fabricating fibre-reinforced plastics. Recently, considerable attention has been paid to it, and it has emerged as one of the most versatile and cost-effective processes used in the composites industry. The use of pultrusion process to manufacture continuous profiles of composite materials is expanding rapidly [37].

The curing an epoxy resin with a mixture of cycloaliphatic amines was studied, and the focus was on the effect of the copolymerization with a commercial PU elastomer. A simplified model was proposed to represent the copolymerization reaction. It considered the effect of the temperature and the concentration of the elastomer on the reaction rate, and it was simple enough to be included in model for processing conditions. A nonlinear regression analysis of the experimental conversion data obtained from differential scanning calorimetry was utilized to find the best fitting parameters to Kamal’s equation for the chemically controlled part of the reaction (short times) under isothermal and constant heating-rate conditions. The Rabinowitch approach together with the Addam-Gibbs theory was utilized to introduce the effect of diffusion control at the end of the reaction on the overall constant for the reaction rate [38].
Electron beam (EB) processing of composites involves using electrons as ionizing radiation to initiate polymerization or cross-linking reactions in suitable substrates, thereby enhancing specific physical and chemical properties. Industrial EB processing of plastics and composites has been an established industry for the last 45 years [39].

Currently, there are about 600 EB accelerators being used worldwide for the processing of plastics [40].

Sasaki et al. (1997) evaluated the combined effects of long-term durability of FRP cables in a maritime exposure test site. Carbon, aramid, glass and vinylon fibre cables were evaluated for tensile strength, modulus, and relaxation under direct sunlight radiation and under saltwater immersion. Each of the six cables was subjected to varying ultraviolet intensity tests either with or without prestressing. The first two cases considering the effects of direct sunlight without prestressing showed no major changes in residual tensile strength. Another case study without prestressing was conducted under submerged condition in seawater without direct expose to UV effects. The composites with the aramid fibre and epoxy resin matrix experienced the most drastic strength reduction, retaining only 49% of the initial value. Also, the glass and vinyl on matrices realized strength degradations of 65% and 71%, respectively. Most of the prestressed CFRP and AFRP obtained from direct sunlight locations experienced less than 30% relaxation losses, while specimens not directly affected by UV rays underwent losses less than 20%. Ultraviolet rays can degrade the efficiency of the fibre composites due to a chemical reaction in the polymer matrix. When used in design of exposed elements, UV-inhibitors can be added to the resin matrix mix before curing [41].
2.4 REINFORCEMENT OF DIFFERENT FILLERS TO POLYURETHANE

Polyurethane elastomers were improved with reinforcement of carbon fibre, glass fibre, silica, mica and calcium carbonate. These composites showed higher moduli and tensile strengths compared to the unfilled polyurethane [42-48].

Polymer composites, commonly present in almost all polymers, are usually incorporated to reinforce their physical properties or to impart certain special functions. In case of polyurethanes, fillers are used to reduce its cost, improve physical properties, and impart certain special functions. Inorganic fillers like glass fibre, glass flake, calcium carbonate, mica, and talc are used to increase mechanical properties like modulus of elasticity, tensile strength, compression strength, shear strength, flexural strength, impact strength and hardness of composite [49-53].

The reinforcement of elastomers with short fibres results in good strength and stiffness for both the soft and tough elastomer matrices. Short fibre reinforced elastomer composites have attracted greater attention due to their better mechanical properties and economic feasibility [54].

The normal reasons for introducing filler to a plastic are to enhance general properties, to introduce specific characteristics and to reduce the cost of the product. Classifications of fillers are generally based on source, performance function, composition or morphology. Fillers may thus be organic or inorganic, and each group comprises fibrous and non-fibrous types. The natural filler materials, which are composed largely of cellulose, are biodegradable polymers. The mechanical properties of filled polymers are determined by the size, shape,
loading, and properties of the filler but more essentially by the interaction of the filler with the surrounding matrix [55].

Fillers have important roles in modifying the properties of various polymers. The effect of fillers on properties of the composite depends on their concentration and their particle size and shape, as well as on the interaction with the matrix. The theory of filler reinforcement of polymers predicts the formation of a boundary layer of a matrix material on the surface of the filler [56-57].

Garnet is used as a filler to give abrading property to PU foam composite. Garnet is an inorganic material having quite high degree of hardness, which can make it applicable as an abrasive and jewel. In practical application, it is used as an abrasive for display panel (cathode-ray tube, liquid crystalline display and plasma display panel) in the powder state [58].

The garnet-filled PU composite, having abrading property is to be applied as an abrasive not in a powder forms. When it is employed in a practical abrasion process, it can make the process simpler and less costly due to the reduction in the quantity of abrasive used. It can also prevent environmental problems because of diminishing use of garnet powder scattered during the process. To study basic physical properties of garnet-filled PU composites, density, hardness, and compression strength were measured as functions of blowing agent content and filler and polyol formulation. Percent volume loss and arithmetical mean roughness were also measured to investigate abrasion properties and the relationship between basic properties and abrasion properties [59].

Glass is an amorphous material made from silica (SiO₂). Unlike window or bottle glass, fibres for reinforcing can achieve very high tensile strengths if the surface
is protected from abrasion, moisture and water vapour. In addition to being highly abrasive to each other, moisture has also been found to have a deleterious effect on the overall strength of glass fibres. Physico-chemical absorption produces local areas of corrosion thus reducing strength properties. This strength reduction is thought to be due to a combination of stress corrosion and a reduction in effective surface energy [60].

Aramid or aromatic polyamide fibres are used to reinforce several polymer matrices, producing composite materials with high tensile strengths and moduli, fatigue resistance, damage tolerance and thermal stability [61].

Applications of aramid fibre-reinforced composites are found in several industries, including aircraft and aerospace, military, marine and sporting goods [62].

Polyurethanes prepared from poly (oxypropylene) glycol (PPG) have lower properties than other polyester glycols based polyurethanes. In order to make PPG based polyurethane elastomers competitive; there is a need to investigate the use of various fillers such as carbon, fibre, glass fibre, plastic particles, and inorganic compounds such as silicate and calcium carbonate for their compatibility with polyurethane.

A number of resins including thermoset (unsaturated polyester, epoxy, phenolic and polyurethane (PU) resins have been used in the pultrusion process [63-64].
2.5 REINFORCEMENT OF GLASS FIBRE TO POLYURETHANE

In glass fibre reinforced polymers, the reinforcement provides the main strength and stiffness; the polymer acts primarily as an adhesive in order to transfer the load between the discrete glass fibres. The polymer also prevents environmental attack of the glass fibres as well as preventing loss of strength due to abrasion. In its capacity as an adhesive the resin acts as a stress medium, so that if a fibre breaks then interfacial shear stresses are developed at the broken ends of the fibre, the axial fibre stress is developed again a short distance from the fractured ends. One would expect the greatest strength when there is good bonding between the glass and the polymer; high strength can also be achieved with comparatively low bond strengths provided the adhesive areas are large. Fibres give a large ratio of adhesive area to cross-sectional area so it should be possible to attain high tensile strengths with most polymeric materials. W.B. Thomas (1972) investigated in the first part it has shown that at comparatively high strain rates, the strength of bonded glass strand is almost independent of the material used as the matrix, and high strengths can be attained with soft waxes and resins [65].

Reinforcement of elastomers with short fibres results in high strength and stiffness for both the soft and tough elastomer matrices. Short fibre reinforced elastomer composites have attracted greater attention due to their better mechanical properties and economic feasibility [66].

Economical E-glass fibres, commonly referred to as fibreglass, are manufactured from lime-alumina-borosilicate glass developed for its high electrical resistance. E-glass fibre polymers are the most widely used in general commercial applications, comprising 80-90% of commercial glass fibre production [67].
2.6 IMPROVEMENTS IN PERFORMANCE OF PU COMPOSITES

The strength of a composite is improved if the polymer content approaches the theoretical minimum. Improvements in PU performance are becoming more and more attractive in many ways, and these are mainly classified into two methods: (1) modification of PU components, and (2) modification utilizing polymer alloy technology. In the former method, the suitable components of PU for effecting high performance are usually polyols because they occupy the highest percentage in PU materials. Although aromatic polyols are considered a good candidate for improving the mechanical and thermal properties of PU elastomers, they create a processing problem due to their high melting points [68-69].

For enhancing PU performance, introduction of thermally stable units such as urea and amide into PU backbones has been extensively examined. Poly (urethane-urea) (PUU) is a family of block-type copolymers with hard segments based on diisocyanates and diamines, and soft segments based on polyols. Superior thermal and mechanical properties of PUU were contributed by both chemical structures and intermolecular force [70-72].

Silicon and titanate coupling agents are used to process the surface of ammonium nitrate (AN) particles in order to decrease the surface tension, improve affinity to the adhesive and adhesive strength of the surface, and to improve the mechanical property of an AN/PU energy composite. A SEM and ESCA analysis shows the effect of coupling agents on the mechanical property of the AN/PU energy composite [73].

A composite has been developed combining PU and a calcium silicophosphate glass ceramic. It has a modulus of elasticity of 2.2 GPa, which is close to that of
cortical bone at (6-20 GPa) thus making it suitable for load-bearing devices such as vertebral column replacement [74].

2.7 EFFECT OF FIBRE REINFORCEMENT ON MECHANICAL PROPERTIES

W.F Thomas (1972) investigated the effect of certain factors on the tensile strength of bonded glass stand. In glass fibre reinforced polymers, the reinforcement provides the main strength and stiffness. The type of material used to bond the fibres together primarily determines the tensile strength of the bonded glass fibre strand. It is also determined to some extent by the length of the test sample and by the extent of strain employed in the test.

The tensile strength of polymer impregnated glass fibre strand is improved by an initial dilution of the resin; the mean breaking stress is dependent on sample length and strain rate.

The tensile strength of glass fibre strand is a function both the gauge length and the diameter of the individual fibre in the strand for the same total cross sectional area. The strength increases with decrease in gauge length and decrease in fibre diameter.

Chin-Hsinc Chen et al. (1992) studied the process developed to manufacture PU pultruded composites. They developed blocked isocyanate (NCO) -terminated PU prepolymer synthesized from t-caprolactam blocked blends of toluene diisocyanate (TDI) and branched polyester [75]. The processability and mechanical properties of various fibres (glass, carbon, and Kevlar 49 aramid fibre) reinforced PU composites have been studied. From the study, it was found

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that the blocked PU prepolymer with chain extender showed excellent processability for pultrusion. They have also studied mechanical properties including tensile strength, specific tensile strength, flexural strength, specific flexural strength, flexural modulus and impact strength.

The Fig. 2.1 shows the tensile strength of pultruded glass fibre, carbon fibre, and Kevlar fibre reinforced PU composites with various fibre contents. Results indicated that the tensile strength increased with fibre volume content and a linear relationship was established between them. CF/PU composites possess the highest tensile strength whereas the GF/PU composites have the lowest [76-77].

The maximum stress transfer rate does not depend on the angle of the fibre to the loading direction and the strain concentration data can be used more closely to predict the strength of short fibre composite [78].
Increasing the concentration of fibres resulted in reduction of tensile strength and tear strength, but increased modulus of the composites [79].

Chopped strand glass fibre reinforced particle-filled polymer composite with different volume fractions of glass fibres have been investigated for tensile strength. Both the properties have been studied with respect to 1 to 10% fibre content. The tensile modulus showed a marked increase from 1111.5 to 1973.0 MPa for unfilled polyester sheets to sheets containing 10% short glass fibres. The composites were inert to most of the chemicals except concentrated sulfuric acid, which damage the surfaces of the composites [80].

The mechanical properties, such as the strength and modulus of short fibre reinforced composites have been shown to depend critically on the microstructure. For short fibre reinforced polymer composites, the microstructure is referred to fibre length, fibre orientation, fibre distribution and fibre matrix bonding [81].

The effect of the fibre and microvoid content on static mechanical properties can be described by approximate formulae based on experimentally determined results. Increasing fibre content induces an increase in the flexural strength and the Young's modulus. Contrarily, increasing microvoid content in the matrix means decrease in the flexural strength and Young's modulus [82].

The effect of fibre volume content on flexural strength and flexural modulus are shown in Fig. 2.2. The higher the fibre volume content means higher the flexural strength and the flexural modulus. CF/PU composite showed the highest flexural strength and flexural modulus followed by GF/PU and then KF/PU.
Becky Abdel-Magid et al. (2003) studied the flexural creep behaviour of the E-glass/PU material and they showed that E-glass/PU exhibit tertiary creep loading to rupture within a few hours when subjected to 75% of its flexural strength at room temperature, and 57% of its flexural strength at 50°C. Typical mechanical properties of the E-glass/PU are tensile strength (1.4-80 MPa) and Young's modulus (0.7-6.9 GPa) [83-84].

The effect of voids on the strength of natural fibre-polyurethane composites showed that increasing fibre content induces an increase in the flexural strength and the Young's modulus. Contrarily, increasing microvoid content in the matrix means that the flexural strength and Young's modulus are decreased. The increase of microvoid content leads to decrease in flexural strength [85].
Composite materials containing E-glass fibre reinforcement tend to be much more sensitive to tensile or cyclic fatigue loading in the fibre direction than composites reinforced with other fibres. Properties of glass fibre polymer reinforcements, on the other hand, have shown a significant rate dependency. It is also apparent that there are no conclusive reasons for this phenomenon [86].

The tensile strength of glass fibre bundles is closely dependent on flaw nucleation and growth from contact abrasion and hydrolytic degradation [87]. The flaws significantly reduce the realizable strength of commercial fibres [88].

Curtis (2000) has mentioned that the rate effect is due to the environmental sensitivity of the glass fibres, rather than any viscoelastic effect. He referred to studies, which have shown that the rate effect changed when the environment surrounding the glass fibres was changed [89].

Studies performed by Mandell (1982) agree with the hypothesis that tensile fatigue failure in glass composites appears to be a fibre dominated failure mode, rather than matrix or interfacial cracking [90].

The reinforcement of thermoplastic polyurethane (TPU) elastomers with Conex and Technora fibres was achieved without any surface treatment or addition of any compatibilizer. Upto a 10 wt% fibre loading, the modulus of the composites was linearly increased with increasing fibre content. Both the moduli at 10% strain (from tensile testing) and the storage modulus (from dynamic mechanical analysis) of the Technora–TPU composite were significantly higher than those of the Conex–TPU composite. This might be due to the fact that the modulus of the Technora fibre was about twice that of the Conex fibre [91].
The untreated short glass fibre reinforcement of unmodified epoxy led to linear flexural behaviour up to the fracture point. Due to the plasticization effect, surface treatment of glass fibres and modification of epoxy resulted in some non-linear plastic behaviour. However, in 30% GF specimens all flexural stress–strain curves were linear due to the higher content of stiff glass fibres [92].

The mechanical behaviour of a unidirectional fibre reinforced composite with 50% vol fraction E–glass reinforced to polymer at low strain rate was investigated; the loading conditions were uniaxial and proportional multiaxial compression with quasistatic strain rate [93].

High mechanical performance and flexibility of epoxy based composites can be achieved by employing short glass fibres treated with a suitable SCA together with rubber (e.g. HTPB) domains dispersed in epoxy matrix, and when the dispersed particle size becomes smaller and more uniform, then flexibility was more improved [94].

PU–polyether-polyimide blend materials, which are prepared by mixing PU and polyamic acid solution followed by low thermal treatment, are a novel type of thermoplastic elastomers which exhibit a well phase-separated morphology, possess a wide range of service temperature and also have good tensile properties [95].

The stress corrosion cracking in a unidirectional E-glass/ polymer composite was subjected to nitric acid solution treatment without mechanical stress initiation on the individual fibre exposed composite surface. The initiation rate of the fibre
The mechanical behaviour of a unidirectional fibre reinforced composite with 50% vol fraction E-glass/vinylester at low strain rates has shown a slight increase in compressive strength. The compressive strength of most fibre-reinforced composites in fibre direction is roughly one-half of their tensile strength. Therefore, the prediction of the compressive strength is a critical issue in designing composite materials and structures [99].
The incorporation of glass fibres into the oil palm fibre composite increased the stiffness of the hybrid composites. Owing to the weak interfacial adhesion between the oil palm fibres and epoxy matrix and the weak nature of the oil palm fibres, the oil palm fibre composite is unable to withstand the applied load transferred from the epoxy matrix resulting in an inferior stiffness property of oil palm fibre composite compared to the glass fibre composite. The enhancement in the stiffness of the hybrid composites with the addition of glass fibres is attributed to the higher tensile modulus of glass fibres, which is about 66-72 GPa than that of oil palm fibre, which has a tensile modulus of about 1-9 GPa. Furthermore, glass reinforced composites exhibit extensive delamination between glass fibre plies. Glass fibres are capable of absorbing high impact energy [100].

Hardness of the Al₂O₃ PUR elastomer composites was higher than the neat PUR elastomer and it increased with increasing content of Al₂O₃ [101].