CHAPTER II

LITERATURE REVIEW

Composites are the materials that are composed of two or more constituent materials (i.e., matrix and filler). These constituents are normally different in both of their chemical and physical properties. The morphology of the minor phase remains separate and distinct in its own entities within the composites. Generally, the reinforcing materials contribute their special physical and mechanical properties to finally enhance the properties of the matrix. Such a synergism produces new properties that are inaccessible from the parent constituents, while a wide variety of the matrix and the reinforcing materials allows researchers and practitioners to design materials with desired properties from materials of diverse origins. Usually, the fillers are in the form of fibers, and the resulting fiber-reinforced composite materials can be divided into two main categories: short fiber-reinforced materials and continuous fiber-reinforced materials. The continuous fiber-reinforced materials often exist in a layered or laminated structure, while both the short and the long fiber-reinforced composites can be fabricated from a variety of processing techniques.

Generally, mechanical properties of the composite materials are anisotropic in nature (i.e., measured properties dependent on direction), because of the local structure, i.e., orientation, of the reinforcing fibers. Composites can fail on the microscopic or macroscopic level, depending on the method of measurement. For examples, in compression, failure usually occurs in the microscopic level where delamination occurs along the interface between the reinforcing fillers and the matrix, while, in tension, failure can occur in either the macroscopic or the microscopic level, or both, through the failure of the matrix in combination with the failure of the matrix. At the microscopic level, the mechanical properties of the composites are dependent upon orientation, state of mix, and interaction of the fibers as well as the inherent properties of both the matrix and the reinforcing materials.

To understand more about the mechanical properties of the composites, some basic concepts and theories are reviewed as follows.

2.1 Dependence of Mechanical Properties on Orientation of Reinforcing Fibers

2.1.1 Slab model

Generally, the reinforcing materials used in the composites are in the fiber form and these fibers may orient randomly within the composites. However, it is also possible to arrange them to achieve the highest properties because the properties of the composites can be determined by the degree of orientation of the fibers as well as the properties of the matrix and the reinforcing materials.
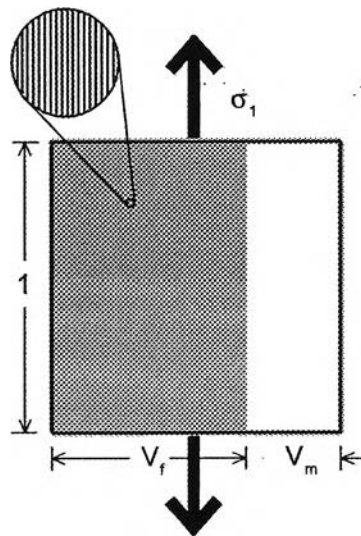

Figure 2.1 Applied force parallel to the fibers axis.

Considering the "slab model," this model idealized by gathering all the fibers together, leaving the matrix to occupy the remaining volume. A typical region of the material contain a volume fraction of uniaxially-aligned fibers (V_f) and then the matrix volume fraction is $V_m = 1-V_f$ In case of applied stress (σ_1) along the fibers direction, the fibers and matrix act in parallel to support the stress so the strain in this case must be the same and can be written as:

$$\varepsilon_f = \varepsilon_m = \varepsilon_1$$

The stress in each phase has to be summed up to arrive at the total stress ($\sigma_1 = \sigma_f + \sigma_m$). Since the stress in each phase has to times with the area or in this case is volume fraction, it can be rewrite as:

$$\sigma_1 = \sigma_f . V_f + \sigma_m . V_m = E_f . \varepsilon_f . V_f + E_m . \varepsilon_m . V_m$$

The modulus is equal to stress divided by strain, so:

$$E_1 = \frac{\sigma_1}{\varepsilon_1} = E_f V_f + E_m V_m$$

This relation is known as the rule of mixing which is used for predicting the overall modulus from the moduli of the constituent phases and their volume fraction.
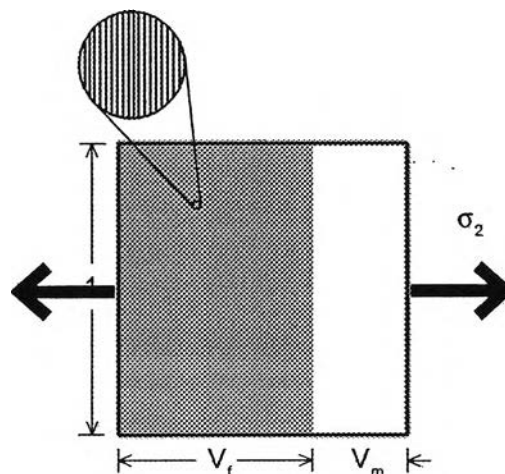

Figure 2.2 Applied force perpendicular to the fibers axis.

When the stress applied in the transverse direction as shown in Figure 2, in this case, stress in both phases is equal so it can be written as:

$$\sigma_f = \sigma_m = \sigma_2$$

$$\frac{1}{E_2} = E_f V_f + E_m V_m = \frac{\sigma_f V_f}{E_f} + \frac{\sigma_m V_m}{E_m}$$

And the overall modulus is equal to stress divided by strain, therefore:

$$\frac{1}{E_2} = \frac{V_f}{E_f} + \frac{V_m}{E_m}$$

The equation of transverse modulus from the series slab model is considered unreliable, because it is hardly agreed with the experiment.

In more complicated cases, reinforcing fibers can be aligned in more than one directions or, instead of the fillers in the fiber form, spherical or irregularly-shaped particulate fillers can also be used. In such cases, the equation obtained from the parallel slap model provides an upper boundary of such composites, while the equation from the series slap model provides the lower boundary, as illustrated in Figure 3.
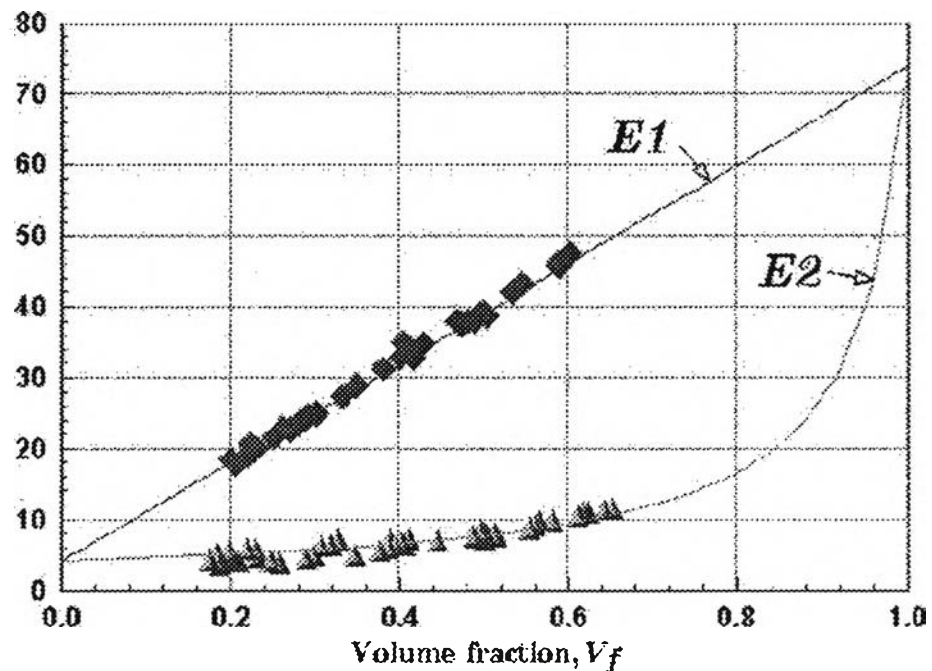

Figure 2.3 Rule-of-mixtures predictions for longitudinal (E_1) and transverse (E_2) modulus, for glass-polyester composite (E_f = 73.7 MPa, E_m = 4 MPa).
Experimental data was taken from Hull (1996).

Most practical cases will be somewhere between these two extreme models and the search for practical models for these intermediate cases has occupied considerable attention in the research community. Perhaps, the most popular model is an empirical one known as the Halpin-Tsai equation, which can be written in the form:

$$E = \frac{E_m \cdot [E_f + \zeta(V_f \cdot E_f + V_m \cdot E_m)]}{V_f \cdot E_m + V_m \cdot E_f + \zeta E_m}$$

Here ζ is an adjustable parameter that results in series coupling for $\zeta = 0$ and parallel averaging for a very large ζ.

2.1.2 Halpin-Tsai Equations

The Halpin-Tsai equations are a set of empirical relationships that enable the property of a composite material to be expressed in terms of the properties of the matrix and the reinforcing phases together with their proportions and geometry. These equations can be curve-fitted to exact elasticity solutions and confirmed by experimental measurements - they work well but the parameter ζ has no scientific basis nor is it related to any material or geometric property. Halpin and Tsai showed that the property of a composite P_c could be expressed in terms of the corresponding property of the matrix P_m and the reinforcing phase (or fiber) P_f using the following relationships:

$$P_c = P_m \left(\frac{1 + \zeta \eta f}{1 - \eta f} \right) \qquad \eta = \frac{\left(\frac{P_f}{P_m}\right) - 1}{\left(\frac{P_f}{P_m}\right) + \zeta}$$

The factor ζ is used to describe the influence of the geometry of the reinforcing phase on a particular property. This factor is different for different properties in the same composite.

Table 2.1 Show the summarizes this factor for many typical geometries

Geometry	E_x	E_y	v	G
Aligned continuous fibers	$fE_f + (1-f)E_m$	$\frac{E_f E_m}{fE_m + (1-f)E_f}$ or $\zeta = 2 + 40 f^{10}$	$fv_f + (1-f)v_m$	$\zeta = 1 + 40 f^{10}$ or $G_m \left\{ \frac{G_f(1+f) + G_m(1-f)}{G_f(1+f) + G_m(1-f)} \right\}$
Spherical particles	$\zeta = 2 + 40 f^{10}$	$\zeta = 2 + 40 f^{10}$	$fv_f + (1-f)v_m$	$\zeta = 1 + 40 f^{10}$

Geometry	E_x	E_y	ν	G
Oriented short fibers	$\zeta < l_c \quad E_m\left(1 \cdot f\left(1 - \frac{l}{2l_c}\right)\right)$ $l \geq l_c \quad f E_c\left(1 - \frac{l_c}{2l}\right) + (1 - f)E_m$	$\zeta = 2 + 40 f^{10}$	$f \nu_f + (1 - f)\nu_m$	$\zeta = 1 + 40 f^{10}$
Oriented plates	$\zeta = 2\left(\frac{l}{t}\right) + 40 f^{10}$	$\zeta = 2\left(\frac{w}{t}\right) + 40 f^{10}$	$f \nu_f + (1 - f)\nu_m$	$\zeta = \left(\frac{l + w}{2t}\right)^{1.73} + 40 f^{10}$
Oriented whiskers	$\zeta = 2\left(\frac{l}{d}\right) + 40 f^{10}$	$\zeta = 2 + 40 f^{10}$	$f \nu_f + (1 - f)\nu_m$	$\zeta = \left(\frac{l}{d}\right)^{1.73} + 40 f^{10}$

In all composite systems the equations are not valid above $f = 0.9$, since these volume fractions of fibers are impossible geometrically.

Empirical and semi-empirical equations like the treatments of Halpin and Tsai (Halpin, 1976), which are widely used in industry can only be useful in reproducing available experimental data.(Hull, 1981; Agarwal, 1990; Tucker, 1999). They always reflect the existing technological level and are not helpful in deciding if the performance of a certain composite can be improved further or not. To make this decision, it is necessary to be able to quantify the degradation effects of imperfections like fiber or platelet agglomerations and their poor adhesion to the polymer. Based on these quantifications one could decide about the potential of further improvements of the properties of the composites by controlling the degree of imperfections. Empirical equations cannot fulfill this task and therefore it is necessary to have another method at hand which can predict the achievable effective properties of fiber- and platelet-reinforced composites.

2.2 Electrospinning process

The electrospinning process is the unique process which was used to produce the non-woven mat with the diameter ranging from nanometer to sub-micrometer. Electrospinning process is simple and versatile process which requires a small amount of the polymer to produce. The concept of electrospinning process is relatively simple to realize in practice. The polymer was dissolve or melt into the liquid phase and place into the capillary tube which is applied a high voltage. When the liquid polymer is charged, electrical forces are inducing into the free charges.

These free charges generate the force in the polymer liquid along the direction of the electrical field. Generally, the polymer liquid will form the sphere at the tip of the capillary due to the surface tension and gravimetric force. Then free charges continue generate and accumulate the force until it overcome the surface tension. This resulting in elongation of the drop and forms a conical shape which well known as "Taylor cone". At the sufficiently electrostatic force, ejection of a continuous stream which usually calls "jet" from the tip of the cone and collect on the collector which connect to the ground. The diameter of the jet is decrease along the movement toward the collector. During the movement of the polymer jet, the solvent begin to evaporate immediately so a good selection for the solvent is necessary. This is because evaporation period is very short so the boiling point of the solvent should not be so high. As the jet keeps moving, the electrical forces in the radial direction overcome the cohesive forces in the polymer jet at a particular position close to the collector. At this point, a single liquid jet is divided into two or more jets with nearly equal charge. This process repeats several times before the liquid reaches the collector forming a lot of thinner jets which repel each other to give rise to random trajectories and lateral velocities. These random thin jets form random fiber orientations on the collector. (Doshi and Reneker, 1995; Fong, 1999)

Both electrostatic and dynamic instabilities can contribute to the basic operation of this process. With the low molecular weight liquids, the fluid usually breaks up into the small droplets (charged droplets). This process is well known as "electrospraying" which widespread commercial success in various applications such as spraying, printing, and agricultural technologies. However, with the polymer fluid, the viscoeleastic forces of polymer stabilize the jet, and permit the small fibers formation. Under certain conditions, electrostatic instabilities are believed to result in the break-up of the main filament into many smaller filaments. This process has been termed "splaying" (Srinivasan, 1996; Reneker, 1996; Doshi, 1995). Although little is currently known about this splaying process, it is thought to be responsible for the unusually small diameter fibers (as small as 40 nm (Reneker, 1996)) which can be produced by electrospinning. The fibers are typically laid down in a random fashion on the collecting screen to form a nonwoven fabric.
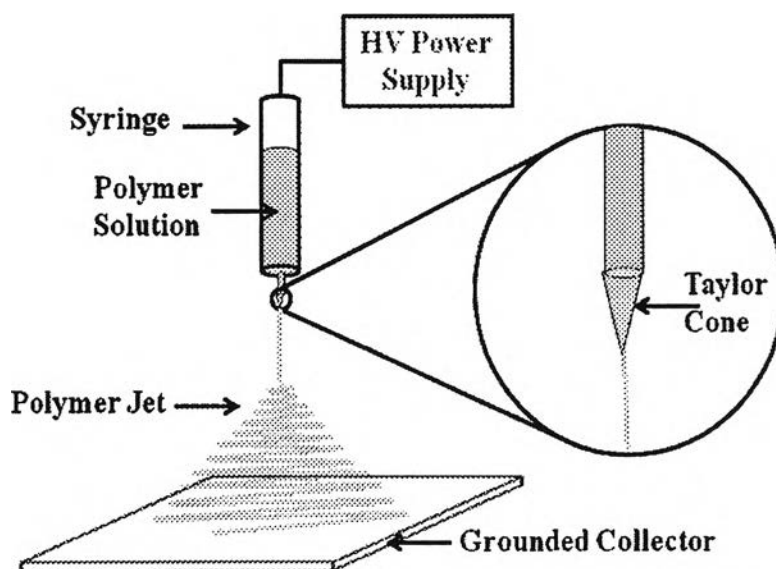
Figure 2.4 The set up of electrospinning process.

In the recent years, this technique was used for the preparation of the polymer nanofibers and metaloxide/ceramic nanofibers. Polymer nanofibers have an especially high surface-to-volume ratio, flexibility in surface functionalities and superior mechanical performance (Reneker 1996; Deitzel, 2001; Shin, 2001; Reneker, 2000). They can be used in a broad range of applications, in particular in tissue engineering (Matthews, 2002), sensors (Wang, 2002), protective clothing (Schreuder-Gibson, 2002), filters (Tsaia, 2002), etc. The nanofibers could be aligned (parallel and cross patterns) when an insulated cylinder attached to the axel of a DC motor is used as substrate (Sundaray, 2004). The separated two pieces of electrically substrate can be use as collector to align polymeric and ceramic nanofibers (Li, 2003). Katta et al. used copper wires spaced evenly in the form of a circular drum as a collector of the electro spun nanofibers (Katta, 2004).