

CHAPTER I

INTRODUCTION

1.1 Background

Polymer blends containing varying amounts of different starches are being investigated as possible replacements for pure synthetic polymers. It is expected that the starch portion will degrade in the environment and this will lead to a decrease in solid-waste pollution. Also, increased use of starch would reduce our dependence on nonrenewable petrochemicals from which synthetic polymers are derived.

1.1.1 Starch

Starch is the major form of carbohydrate storage in green plants. Starch is a polymer that consists of six-member-ring glucose units (glucopyranose). It is a mixture of amylose and amylopectin polymers. Amylopectin has an α -1-4 linked backbone and about 5% of α -1-6 linked branches. Branch chains in amylopectin are arranged in clusters, and the branch-chain length varies with the species structure. Amylose is a primary linear molecule that has low branches. The molecular weight of amylose is of the order of several hundred thousand, while that of amylopectin is several million. In normal starches the major fraction is amylopectin, however, specially hybrid starches may contain up to 70% amylose.

Native starches are present in semicrystalline granular forms with densities of 1.5 g/cm^3 . Although starch is not thermoplastic in the dry state, since the glass transition temperature (T_g) and the melting temperature (T_m) occur above the decomposition temperature (above 175°C), it does form a melt in the presence of a “ plasticizer ” such as water. The stepwise elimination of substantially all native starch structure in the presence of a controlled amount of water is known as starch destructuring and is only achieved with the correct use of a combination of water, heat, and shear. The T_g of starch is a function of water content.

Starches isolated from different botanical sources differ in their chemical structure and morphology. Some starch granules, such as amaranth and pigweed, have submicron sizes, whereas others, such as canna and potato, can have diameters larger than $100 \mu\text{m}$. Many starches, such as potato and canna, are of oval shape; maize, oats and rice starches are of polygonal and round shapes; wheat and barley starches are disk shaped. Blends made from starches with different amylopectin and amylose ratio, shape, and size would be expected to have considerably different physical properties.

Starch by itself is unsuitable for most uses as a plastic. It is difficult to process and is extremely sensitive to humidity. Depending on the environment, the physical properties such as elasticity, hardness, and dimensional stability are greatly affected. To overcome the problems caused by the poor physical properties of pure starch, it is often blended with water insoluble synthetic polymers. The technique of blending two or more components to form a composite material having new characteristics is a well-known procedure in the synthetic polymer industry. Because hydrophilic starch and hydrophobic synthetic polymers are immiscible at the molecular level, simple mixing produces blends that tend to phase-separate. One means by which compatibility between two immiscible polymers can be improved is by

introducing a reactive functional group on each polymer. The functional group is expected to react during blending.

1.1.2 Rheology

Rheology is the study of the deformation and flow of materials, whether in liquid, melt, or solid form, in terms of the material's elasticity and viscosity.

- Elasticity

Elasticity is the ability of a material to store deformational energy, and can be viewed simply as the capacity of a material to regain its original shape after being deformed.

- Viscosity

Viscosity is a measure of a material's resistance to flow and reflects the material's rate of dissipation of deformational energy through flow.

- Viscoelasticity

Materials respond to an applied external force or displacement by exhibiting either elastic or viscous behavior or through a combination of these, called viscoelastic behavior. The mechanical properties of viscoelastic materials show a marked time- and temperature-dependence. Most polymeric materials exhibit viscoelastic behavior.

1.1.2.1 Viscous Behavior. When most materials are subjected to a constant shear rate at a fixed temperature, a corresponding steady-state value of shear stress is soon established. The steady-state relation between shear stress and shear rate at constant temperature is known as a flow curve. Shear viscosity is defined as the ratio of shear stress to shear rate.

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (1.1)$$

where

η	=	shear viscosity
τ	=	shear stress
$\dot{\gamma}$	=	shear rate

For Newtonian fluids, the shear stress is directly proportional to the shear rate, so the viscosity is constant. The flow behavior will follow Newton's law,

$$\tau = \eta \dot{\gamma}$$

or

$$\log \tau = \log \eta + \log \dot{\gamma} \quad (1.2)$$

Many nonpolymer fluids, such as gases, water, and toluene, are Newtonian fluids. This type of flow behavior would be expected for small, relatively symmetrical molecules, where the structure and/or orientation do not change with the intensity of shearing.

An arithmetic flow curve for a Newtonian fluid is a straight line passing through the origin with a slope equal to η . A logarithmic flow curve will be a line of slope unity for a Newtonian fluid (Fig.1.1).

For non-Newtonian fluids, since the shear stress is not directly proportional to the shear rate, the viscosity is not constant. Plots giving viscosity as a function of shear rate are an equivalent method of representing a material's viscous shearing behavior. The dependence of shear stress on shear rate can be described by a power law,

$$\tau = k \dot{\gamma}^n$$

or

$$\log \tau = \log k + n \log \dot{\gamma} \quad (1.3)$$

where

k = consistency

n = power law index

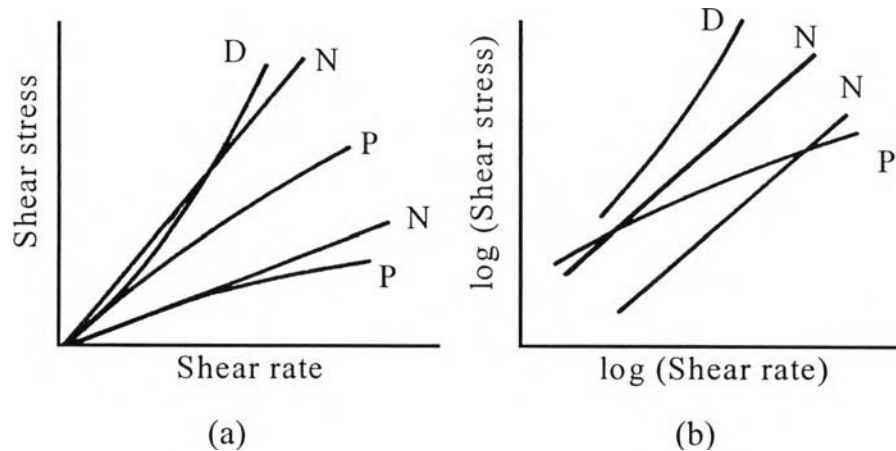


Figure 1.1 Types of flow curves : (a) arithmetic, (b) logarithmic.
N = Newtonian, P = Pseudoplastic, D = Dilatant.

Both dilatant (shear-thickening) and pseudoplastic (shear-thinning) fluids are non-Newtonian fluids. On log-log coordinates, a power-law fluid is represented by a straight line with slope n . Thus, for $n = 1$, it reduces to Newton's law, for $n < 1$ the fluid is pseudoplastic, and for $n > 1$ the fluid is dilatant. Dilatant behavior is reported for certain slurries and implies an increased resistance to flow with intensified shearing. Polymer melts and solutions are invariably pseudoplastic, that is, their resistance to flow decreases with the intensity of shearing.

Viscosity is the most common rheological property used to characterize a polymer. Like other rheological properties the viscosity depends on two main factors. First is the flow conditions which consist of the shear rate, temperature, and pressure. Second is the polymer characteristics such as the chemical structure of the polymer, the molecular weight distribution of the

polymer, the presence of long chain branches, and the nature, type, and concentration of additives and/or fillers.

The flow behavior of suspensions of rigid particles in liquids is important in blend systems. There are at least two reasons for this importance : (1) many fabrication techniques for blends involve the flow of suspensions of liquids, i.e. molten polymers; and (2) most of the theories of the moduli of blends have their origin in the theories of the viscosity of suspensions.

The theory of blend systems start with Einstein's equation for the viscosity of a suspension of rigid spherical particles.

$$\eta = \eta_1 (1 + k_E \phi_2) \quad (1.4)$$

where	η	=	viscosity of the suspension
	η_1	=	viscosity of the suspending liquid
	ϕ_2	=	volume fraction of the rigid particles
	k_E	=	Einstein coefficient

The viscosity of the suspension is related to the viscosity of the suspending liquid and the volume fraction of the filler. The theory ignores all higher-order terms in ϕ . In blended polymers, subscripts 1 and 2 refer to the matrix or continuous phase and the dispersed phase, respectively. Einstein's equation only holds for rigid particles in extremely low concentrations. Over a hundred equations have been proposed for quantifying the viscosity of suspensions of spheres up to moderate or high concentrations.

1.1.2.2 Elastic Behavior. Whenever a force is applied to a solid material, that material will deform in response to the applied force. The most common types of force are a pulling force (called tensile force), a pressing or pushing force, on the end of a columnar sample (called compressive force),

a pressing or pushing force on the side of a long sample (called a bending or flexural force), a rotational force (called a torsion force), or a combination pushing force with a sliding force (called shear force).

If only small deformations are considered and the solid material returns to its original shape when the force is relieved, then the deformation is called elastic. In elastic deformations all of the mechanical energy that is put into the material by the applied force is held within the material and is subsequently used to cause the material to return to its original shape and position, when the applied force is removed.

Hooke's law is used to describe the elastic behavior of an ideal solid, relating the applied stress to the resultant strain through a proportionality factor called the modulus,

$$\begin{aligned} \sigma &= E\varepsilon && \text{(tension, bending)} \\ \text{or} \quad \tau &= G\gamma && \text{(shear)} \end{aligned} \quad (1.5)$$

where

$$\begin{aligned} \sigma, \tau &= \text{stress} \\ \varepsilon, \gamma &= \text{strain} \\ E, G &= \text{modulus} \end{aligned}$$

The modulus is a measure of the material's stiffness or rigidity i.e. its ability to resist deformation. The linear region in which the modulus does not change when the stress is changed is called the Hookean region of the material as shown in figure 1.2.

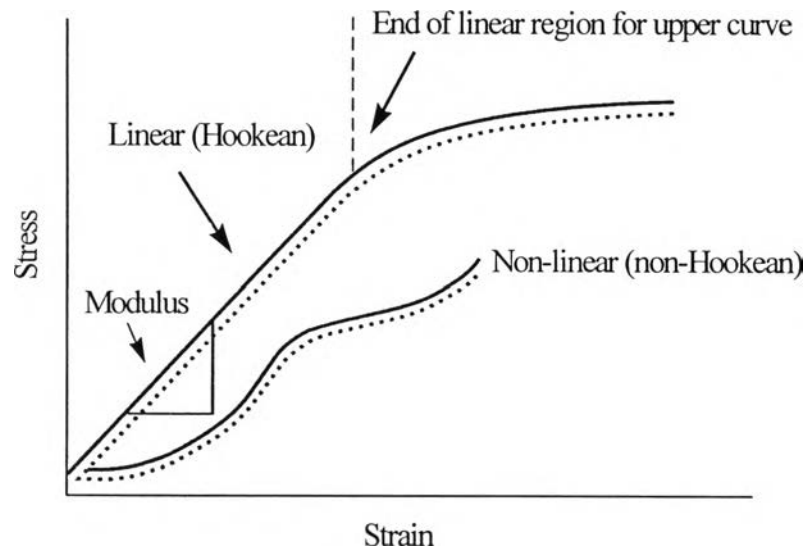


Figure 1.2 Stress-strain relationships for elastic solids.

If the stress and strain are not directly proportional, the material is said to be non-Hookean. The non-Hookean modulus is not constant and is defined only at specific points on the curve using calculus as the derivative of the stress to the strain. In both the linear and nonlinear cases the material returns to its original shape and position when the force is relieved, so the material is elastic.

1.1.2.3 Viscoelastic Behavior. Most polymeric materials have some characteristics that are similar to viscous liquids and some that are similar to elastic solids. These materials are therefore known as “viscoelastic”. Viscoelastic materials can be either liquid or solid, although the distinction between liquids and solids in these materials is not clearly defined. These materials show not only strain and strain rate dependence, but also time dependence. This is apparent in the recovery behavior of viscoelastic materials when compared to Hookean and Newtonian materials (Fig. 1.3).

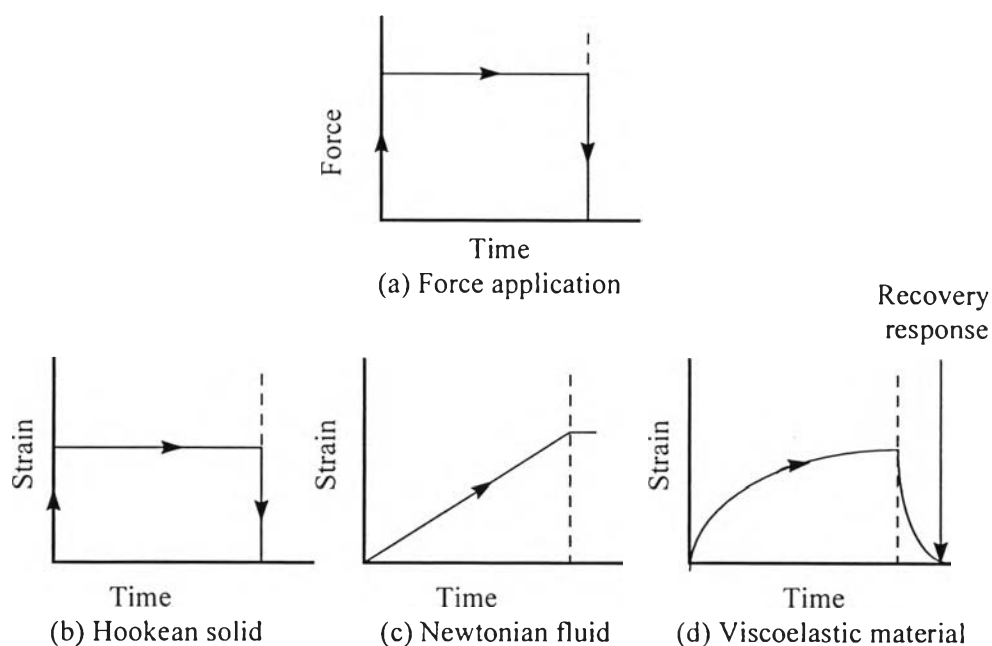


Figure 1.3 Deformational and recovery behavior of a Hookean solid, a Newtonian fluid, and a viscoelastic material.

A Hookean solid under a constant stress deforms immediately to a constant strain, then recovers instantly and completely when the stress is removed. A Newtonian fluid deforms continuously while a constant stress is applied but does not recover when the stress is relieved. A viscoelastic material combines both of these behaviors, showing a time-dependent but incomplete recovery.

In a dynamic mechanical test, an oscillatory strain is applied to a sample and the resulting stress developed in the sample is measured.

For a Hookean solid, the resulting stress and strain signals are in phase. If the sample is a Newtonian fluid, then the stress is proportional to the strain rate (Newton's law). In this case, the stress signal is out of phase with the strain signal, leading the strain signal by 90° . The stress signal generated by the viscoelastic material can be separated into two components: an elastic stress that is "in phase" with the strain, and a viscous stress that is in phase

with the strain rate or 90° “ out of phase ” with the strain. Fig.1.4 shows the behavior of elastic, viscous, and viscoelastic material.

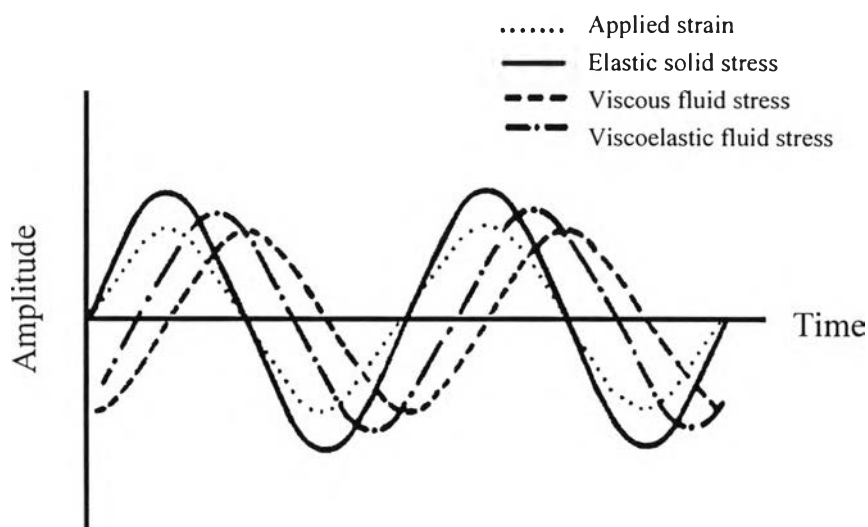


Figure 1.4 The schematic stress response of an elastic, a viscous, and a viscoelastic material to a sinusoidally applied strain.

The elastic and viscous stresses are related to material properties through the ratio of stress to strain, which is the modulus,

$$G' = \frac{\tau'}{\gamma}$$

$$G'' = \frac{\tau''}{\gamma} \quad (1.6)$$

where

$$\tau' = \text{elastic stress}$$

$$\tau'' = \text{viscous stress}$$

$$\gamma = \text{applied strain}$$

$$G' = \text{storage modulus}$$

$$G'' = \text{loss modulus}$$

The storage modulus is a measure of energy stored and recovered per cycle while the loss modulus is a measure of energy dissipated or lost per cycle. The ratio of the loss modulus to the storage modulus is the tangent of the phase angle shift (δ) between the stress and the strain,

$$\tan \delta = \frac{G''}{G'} \quad (1.7)$$

This measures the damping ability or internal friction of the material. It has important implications in terms of the performance of a material.

1.1.3 Microstructure

Microstructure of materials must be understood in order to develop relationships between the structure and properties of materials. The morphology of polymers is determined by a wide range of optical and electron microscope techniques. In polymer blend systems, the micrographs can illustrate the dispersion of dispersed phase and the adhesion between dispersed phase and continuous phase.

1.2 Literature Survey

Griffin *et al.* (1973) reported that starch can be incorporated into low density polyethylene (LDPE) film to impart biodegradable properties. The

degradation rate of starch-based HDPE blend films containing 6-10% of starch was accelerated by adding an autooxidant such as an unsaturated acid to the system.

Otey *et al.* (1976) reviewed the current and potential applications of starch products in plastics. They evaluated starch as an inert filler in poly (vinyl chloride) (PVC) plastics, as a reactive filler in rigid urethane foams, and as a component in poly (vinyl alcohol) (PVA) films. Tensile strength remained good even with as much as 50% starch in the plastic compounds. Clarity of the plastics was also good except for those made by dry blending, but elongation decreased rapidly as the starch level increased.

Faulker *et al.* (1977) studied the rheological and mechanical behavior of glass bead filled polypropylene using a rotation rheometer to obtain low shear rate data and a capillary rheometer for high shear rate data. They concluded that under steady state viscosity conditions the relative shear viscosity was a nonlinear function of the volume fraction of beads at constant shear rate. The relative viscosity decreased with increasing shear rate.

Kataoka *et al.* (1978) used a cone-and-plate viscometer to measure the viscosity of filled polymer melts at fairly low shear rates. Particles used were glass beads and glass balloons. The polymers used were polyethylene and polystyrene. It was found that the relative viscosity was obtained asymptotically even for highly filled material. The relationship between relative viscosity and volume fraction of filler was presented by equations derived by Maron and Pierce, and by Mooney. Only the distribution of particle sizes showed a strong effect on the relative viscosity at a defined concentration.

Otey *et al.* (1987) prepared blend films incorporating starch in a PE matrix and found that the content of starch in starch-based films can be increased without affecting the physical properties of the films by adding urea and a polyol to the starch-poly (ethylene-co-acrylic acid) (EEA) system.

Vergnes *et al.* (1987) studied the rheological behavior of molten corn starch with a pre-shearing rheometer. The results showed that the dependence of viscosity on the shear rate can be described by a power law equation in which the power-law parameters depended on temperature, moisture content, and thermomechanical treatment. Their results indicated that the viscosity decreased when the temperature and water content increased for a fixed thermomechanical treatment. Viscosity decreased with increasing intensity of treatment, and the effect was more pronounced at higher temperatures.

Maiti *et al.* (1991) studied the melt rheology of a blend of styrene-acrylonitrile (SAN) and polypropylene (PP). SAN copolymer formed a two-phase blend with PP with good dispersion of the SAN droplets in the PP matrix. The droplets showed a remarkable tendency to elongation, and the droplet size increased with increasing SAN content of the blend. The melt of PP-SAN blend was found to be pseudoplastic at temperatures below 250°C, with little variation of pseudoplasticity with SAN content. The SAN droplets caused an ease of flow due to their tendency to elongate and alignment in the flow direction. The reduction in melt viscosity was accompanied by a lowering of the activation energy for viscous flow. Melt elasticity of the blend also decreased with increasing SAN content, and its variation with shear rate showed two distinct slopes of plots between recoverable shear strain and shear rate, suggesting a critical shear rate above which the SAN droplets acquired shapes suitable for good elastic recoverability.

Line-Hwa Chu *et al.* (1993) investigated the correlation of viscosity-morphology-compatibility of polymer blends. Polystyrene (PS), polybutadiene (BR), and styrene/butadiene triblock copolymer (SBS) were studied. The viscosity of a polymer blend is influenced by the composition, viscosity ratio between components, interfacial interaction, and morphology. For the PS/BR, the interaction between the PS and BR phases was weak ; the viscosity-

composition curve exhibited negative deviation. For the SEM micrographs, both dispersed and continuous phases were observed. The domain size of dispersion for the PS/BR blend was quite large as compared with that for the PS/SBS and BR/SBS blends. For these two blends, the interaction between the PS and BR phases was mainly due to the chemical bondings existing in the SBS and the viscosity-composition curves were S-shaped. The two phases in the PS/SBS blend appeared to be interlocked. In the BR/SBS blend, the domain size of dispersed phase that was the styrene phase was uniform and small. Although the blending methods had some effect on the morphology of the blends due to the difference in the extent of mixing, the effect on the viscosity curve was insignificant.

Silverstein *et al.* (1994) examined the effects of various calcium carbonate filler types on the ductility of filled amorphous copolyester. One of the calcium carbonate fillers had received a surface treatment. For all filler types, the Young's modulus increased with increasing filler content and was satisfactorily described by Kerner's equation. The only filler to affect the yield stress was the surface-treated calcium carbonate; in this case, the decrease in yield stress was attributed to cracking and splitting of aggregated particles. A sharp drop in fracture strain was observed with increasing filler content.

Gahleitner *et al.* (1994) presented a comparative study of rheological and mechanical properties of polypropylene compounds with talc as a mineral filler. It was concluded that the maximum strength and the terminal relaxation time increased with increasing talc content. The effect of the talc led to an increase in brittleness with increasing talc content. As the talc loading was constant, an increase in interaction between PP and talc improved both flexural and impact properties of the compounds. The variation of the particle size and degree of dispersion of talc resulted in differences in relaxation time spectra and mechanical properties.

Willett *et al.* (1994) studied the mechanical properties of composites of granular starch and low density polyethylene (LDPE) as functions of starch volume fraction, granule size, and presence of compatibilizer. Results were interpreted in terms of theories developed to describe the elongation, tensile strength, and modulus of filled composites. The elongation and tensile strength decreased with increasing starch volume fraction in agreement with theoretical predictions, although the proportionality constants were lower than prediction. The composite modulus increased with increasing starch volume fraction. The addition of ethylene-co-acrylic acid copolymer (EAA) compatibilizer had no effect on elongation and tensile strength, but significantly increased the composite modulus. Composites with potato starch, which have larger particle sizes than cornstarch, had lower tensile strength and moduli than corresponding cornstarch/LDPE composites ; particle size had no effect on elongation.

Marcelo *et al.* (1995) studied the rheological properties of thermoplastic starch and starch/poly (ethylene-co-vinyl alcohol) blends. As in starch-based food materials, the viscosity had an Arrhenius dependence on temperature, an exponential dependence on moisture content and a power-law dependence on shear rate. The power law exponents from the starch blends were less than unity, indicating that the melts exhibited shear thinning. Results on the starch/poly (ethylene-co-vinyl alcohol) blends indicated that the viscosity decreased with decreasing amylose content or increasing poly (ethylene-co-vinyl alcohol) content. The shear-rate dependence increased with an increase in the amylose content of blends.

Vaidya *et al.* (1995) studied the dynamic mechanical properties and morphology of starch and anhydride functional polymer blends. Starch/ethylene-propylene-g-maleic anhydride (EPMA) blends showed two distinct glass transitions in storage modulus and loss modulus plots, one corresponding to the starch and the other corresponding to EPMA.

Starch/styrene maleic anhydride (SMA) blends exhibited one broad transition, since the glass transition temperatures of starch and SMA were in close proximity to one another. The starch in the blend was sensitive to the processing conditions used. Increasing the mixing time from 10 to 20 min and increasing the mixing speed from 50 to 100 rev min⁻¹ resulted in increased melting of the starch granules. Increasing the mixing speed and mixing time also resulted in increased degradation of starch, as evident from gel permeation chromatography.

Bhattacharya *et al.* (1995) blended corn starch (with different amylopectin to amylose ratios) with styrene maleic anhydride copolymer (SMA) and ethylene-propylene-g-maleic anhydride copolymer. Tensile strength and water absorption correlated well with the torque generated during blending : the higher the torque, the lower the tensile strength and the higher the water absorption. The tensile strength of the blends containing SMA decreased when the humidity increased. Fractured surfaces of starch/SMA blends exhibited brittle failure ; for the ductile starch/EPMA blends, shear tearing appeared to be the major failure mechanism. For blends containing EPMA, the percentage elongation increased with increased humidity. Dynamic mechanical analysis of the blends showed two sharp peaks for the tan δ versus temperature plot for starch/EPMA, but showed a single peak for starch/SMA blends.

1.3 Objectives of Research

- To study the effect of starch contents on the rheological properties and morphology of starch-based HDPE blends.
- To compare the rheological properties and morphology of tapioca starch-based and rice starch-based HDPE blends.
- To study the effect of temperature on the viscous behavior of starch-based HDPE blends.