

CHAPTER I

INTRODUCTION

Recently, polymer blends have generated a great deal of research interest in both academic and industrial laboratories throughout the world because of the ease with which polymer properties can be modified to achieve a desired set of characteristic properties such as processing, toughness, barrier properties and chemical resistance that cannot be achieved by simple copolymerization. (Favis *et al.*, 1988 and Bordereau *et al.*, 1992). Synergistic/additive properties of blend components can also be expected from the blends (Mohanty *et al.*, 1995) and in some instances, blending also affords a cost advantage as well. Thus, the production of polymer blends has become a frontier area of research and development activity in polymer technology for the past two decade. The miscible polymer blends are generally characterized by the occurrence of a negative free energy of mixing, which is rare in the case of high molecular weight polymers (Mohanty *et al.*, 1995). Therefore, miscible polymer blends will be formed if there are some specific intermolecular interactions between polymer pairs such as hydrogen bonding (Kleintjens *et al.*, 1986). On the other hand, many random copolymers have been reported to be miscible with homopolymers in spite of the absence of specific interactions (Chiou *et al.*, 1982).

Blends may be miscible (single phase) or immiscible, often with the target property dictating the optimal morphology. (Landry *et al.*, 1994) Miscible polymer blends are generally characterized by occurrence of a negative free energy of mixing, some miscible ternary blends were developed with the concept that polymer A, which is immiscible with each of polymer B and C, can compatibilize the immiscible binary pair B and C. Only few miscible ternary polymer blends have been reported although many miscible binary blends have been found over the last decade. (Jo *et al.*, 1991)

Numerous techniques used to determine if a polymer is single or multiphase may be categorized as under the following:

1. Transparency - Discontinuous domains in polymer blends are often large enough to refract light, forming a translucent or opaque blend when two transparent polymers are mixed. In a miscible one-phase blend of two amorphous polymers, no domains are present to refract light, and hence the blend may be transparent.(Fox *et al.*, 1985) For example, in applications where optical clarity is needed, thermodynamic miscibility between blend components is usually required owing to turbidity that often arises from phase separation. (Landry *et al.*, 1985). Hence if two amorphous polymers give a material, which is not transparent, then the two components are not miscible; however the reverse does not necessarily hold. In semicrystalline materials, this test has limited utility since the crystalline domains may be the source of scattering.

2. Glass-transition temperature, T_g . - T_g of a polymer is the temperature at which the molecular chains have sufficient energy to overcome attractive forces and move vibrationally and translationally. The number and locations of the T_g s provide much insight into the nature of the polymer blend. A miscible one-phase blend should have only one T_g , whereas a two-phase blend should have two T_g , one for each phase. DSC or dynamic mechanical analysis can be used to quantify this property, with the latter being preferred because of increased sensitivity to the glass transition, as well as the opportunity to measure at different frequencies.

3. Other techniques: Other techniques such as light, x-ray and neutron scattering or NMR provide much insight into the blend morphology. (Fox *et al.*, 1985) In addition, in some cases electron microscopy can also be used.

The purpose of this study is to determine properties of blends of a new terpolymer with the trademark ESCOR[®], and poly(acrylic acid).

1.1 Materials

1.1.1 ESCOR[®] Terpolymer

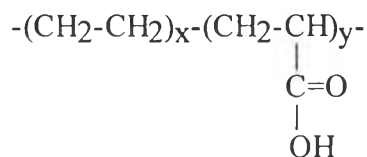
ESCOR[®] terpolymer is a random terpolymer of ethylene, acrylic acid and methyl acrylate. Typical mass fractions are 80% ethylene, 10% acrylic acid and 10% methyl acrylate. The properties of ESCOR[®] terpolymers are described below:

ESCOR[®]310 – provides excellent adhesion to a variety of polar and non-polar materials. For example, ESCOR[®]310 can be used as an adhesive film for industrial laminations or to bond elastomers to fabrics and metals. It can also be used for extrusion coating/laminating and co-extrusion applications where bonding of polar to non-polar materials is critical. It delivers the highest service temperature and modulus of all the ESCOR[®] acid terpolymer. It is used as heat-activated adhesive sealant compounds, TPOs with improved adhesion to metal parts, engineering thermoplastic impact modifier, and compatibilizer for polar and non-polar polymers.

ESCOR[®]320 – provides excellent adhesion to a variety of substrates and other film components, such as aluminum foil, polyolefin, polycarbonate, PET, etc. Applications for these terpolymers are tie resin for blown film, tie resin for extrusion coating and laminating, OPP/ESCOR[®]320/nylon laminates, and PE/ ESCOR[®]320/aluminium foil laminates.

ESCOR[®]325 – provides excellent adhesion to a variety of polar and non-polar materials. It provides the highest melt index and is the softest of all of the ESCOR[®] acid terpolymer. As a modifier, ESCOR[®]325 improves toughness, flexibility and the adhesion characteristic of plastic compounds. Applications are engineering thermoplastic impact modifier, compatibilizer for dissimilar polymers, adhesion promoter for insert molded polyolefin parts, and heat activated seals.

1.1.2 Ethylene Acrylic Acid Copolymer (EAA)



Acrylic acid contains a carbonyl group that will easily give up a hydrogen ion (H⁺) to a chemical that will accept hydrogen ions. In the bulk material, a substantial amount of hydrogen bonding is present, which helps increase toughness vs. poly(ethylene) as described earlier. This acid group is also responsible for the high adhesion of these copolymers to a variety of surfaces.

As would be expected from the presence of a polar pendent group, the bondability (i.e the ability to join two pieces of E-AA film together with heat) of EAA is high. Crystallinity is lower than in PE and hence film clarity is higher. EAA films are more resistant to oils and greases than PE but is more permeable to water vapor. They are, therefore, another choice for food packaging films and shrink-wrap

1.1.3 Ethylene Methacrylic Acid Copolymer (EMAA)

The carboxyl groups in the chain disrupt the linearity of the polyethylene backbone. This interferes with chain alignment and reduces the total crystallinity, as a result, lower melting temperature, stiffness and tensile yield strength in proportion to the acid comonomer content. In addition, the carboxyl functionality contributes to improved adhesion and toughness, with good adhesion to foil, paper, glass, aluminum, and other metals. The degree of adhesion is related to the acid comonomer content. The acid functionality allows the polymers to form very strong bonds to polar substrate.

Toughness, measured by impact resistance, is outstanding compared with LDPE. This increases with acid content and is maintained at

low temperature as the same trend as environmental stress crack resistance. Adding the polar comonomer improves resistance to grease and oils.

1.2 Mechanical Properties

Most plastic materials are used because they have desirable mechanical properties at an economical cost. Mechanical properties, among all the properties of plastic materials, are often the most important properties because these properties are important in virtually all service conditions and end-use applications.

The basic characteristics of the mechanical properties of solids are usually determined by the tests resulting in variation deformation vs stress dependencies, such as stress-strain diagrams. Examination of such dependencies readily brings out characteristics of elasticity, plasticity and strength. (Rosato *et al.*, 1993)

These include both destructive and non-destructive tests. The destructive tests such as tensile testing. Non-destructive tests may vary from visual examination and weight, gloss or hardness tests. (Hunt *et al.*, 1993)

1.2.1 Tensile Strength

The tensile test is the most widely employed test to characterize the mechanical properties of materials like plastics, metals and wood. Tensile tests measure the force required to pull a sample at constant speed and also determine to what extent the materials stretch before breaking. From any complete test record one can obtain important information concerning materials' elastic properties, the character and extent of its plastic deformation, yield strength, tensile strength and toughness.

Stress (σ) is defined as the force applied per unit area of a test specimen. Strain (ϵ) is the ratio of the elongation to the gauge length of the

test specimen or change in length per unit of the original length. Tensile modulus (E) is the ratio of stress to strain at the limit of an infinitely small strain. E is also known as Young's modulus. The tensile strength (TS) is defined as the stress required to break the specimen, while the toughness is the area under the stress-strain curve. Finally the yield strength is defined as the maximum in a stress-strain curve that occurs before the sample breaks. A polymer may or may not have such a maximum.

1.2.2 Hardness

Hardness is not a fundamental property of materials. The term hardness may be defined in more than one way. It may be regarded as the resistance of materials to deformation, particularly permanent deformation, or the resistance of materials to abrasion, indentation or scratching. Hardness values used in this experiment called as a durometer. A typical durometer is a compact hand-held device in which a round indenter is pressed into the material surface under the action of a spring or weight and a pointer registers a hardness value on a graduated scale. The deeper the penetration, the softer the materials.

As a general rule, as the hardness value increases, so do properties such as tensile strength. Hardness testing, which is a rapid and relatively simple process, is used frequently as an approximate means for assessing the tensile strength of materials.

1.3 Rheological Measurements

Rheology is the science of deformation and flow of matter. It concerns with the response of materials to a mechanical force. That response may be irreversible flow, reversible elastic deformation, or a combination of both. The rheological properties of elastic solid may be studied by applying a stress and

measuring the deformation of strain. By subjecting a polymer specimen to an oscillatory stress and determining the response, both elastic and viscous or damping characteristics can be obtained.

1.3.1 Shear Measurements

The shear stress modulus can be represented by a complex dynamic modulus G^* , which is the ratio of the complex stress and complex strain:

$$G^* = \sigma^* / \gamma^*$$

The dynamic modulus can be resolved into two components:

$$G^* = G' + iG''$$

$$\text{Where } |G^*| = \sqrt{(G')^2 + (G'')^2}$$

$$\text{And } G' = G^* \cos \delta$$

$$G'' = G^* \sin \delta$$

Where G' and G'' are storage moduli and loss moduli respectively.

The ratio of G'' and G' also give measure of damping called the dissipation factor or internal friction or damping or loss tangent, is the ratio of energy dissipate per cycle to the maximum potential of stored during a cycle:

$$\tan \delta = G'' / G'$$

Melt rheology depends greatly on temperature and hence any comparison must be made on the basis of comparable temperature. The reference temperature to make this comparison between two dissimilar materials is a matter of some concern. For amorphous materials, usually the glass transition temperature, T_g , is selected as the reference temperature. For semicrystalline materials, the equilibrium melting temperature, i.e. the melting temperature that would be measured if the sample were 100% crystalline and of infinite molecular weight is typically the appropriate temperature to choose.

The choice of temperature at which the melt is most commonly processed is of course determined by the processing equipment and application in question.

1.4 Dynamic Mechanical Properties

Tensile or flexural geometries are used to measure solids, and these experiments are often dynamic mechanical experiments because the typical experiment is to choose one frequency and vary the temperature, rather than vary the frequency at a given temperature. The dynamic modulus (E'), the loss modulus (E''), and $\tan \delta$ are typically reported for these measurements.

The dynamic modulus indicates the inherent stiffness of material under dynamic loading conditions. $\tan \delta$ is a measure of the mechanical damping or internal friction and indicates the amount of energy dissipated as heat during the deformation of material.

The investigation of the dynamic modulus and internal friction over a wide range of temperatures and frequencies has proved to be very useful in studying the structure of high polymers and the variations of properties in relation to performance. These dynamic parameters have been used to determine the glass transition region, relaxation spectra, molecular orientation, cross linking, phase separation, structural or morphological changes resulting from processing, and chemical composition of polymer blends.

The dynamic mechanical properties of polymer blends are determined primarily by the mutual solubility of the polymers. If polymers are compatible and soluble in the others, the properties of the blends are nearly the same as those of a random polymer of the same composition. However, many mixtures of polymers form two phases, due to insolubility of polymers. In this case, the damping temperature curve shows the peaks; each peak is characteristic of the glass transition temperature of one of the components. The steps in the

dynamic modulus temperature curve are characteristic of an immiscible phase system (Murayama, 1982).

1.3.3 Vibration Damping

Once application for the ESCOR[®]/EAA is in vibration damping materials. There is likely to be vibration with rotating or reciprocating machinery, and plastics can assist in vibration damping. Any panel or thin shell structure that is part of the machine can be excited to resonate in bending at a relatively low frequency. Unacceptable levels of noise may be generated because of the large area of the panel. The machine maybe redesigned and metal panels maybe replaced with plastic. The $\tan \delta$ value rises from 0.001 (metals) to 0.01-0.02 for structural plastic, and this maybe enough to reduce the vibration levels. However, there may need to be a metal panel for stiffness reasons, or to contain an environment like hot oil that would attack plastics. In this case a layer of plastic can be applied to one side of the metal panel, or the plastic can be sandwiched between the main panel and a thin metal skin (as shown in figure 1).

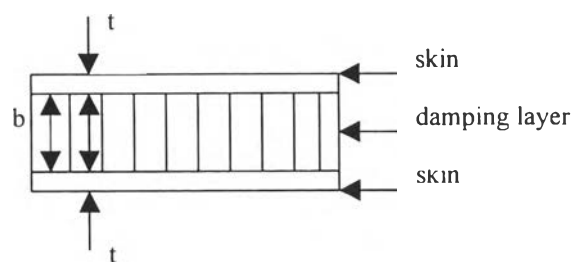


Figure 1 Damping the vibration using a high loss plastic layer plus a stiff metal skin.

1.5 Objectives

1.5.1 To study the ESCOR[®] terpolymers and EAA blends on their miscibility.

1.5.2 To determine blend properties by looking at mechanical, rheological and dynamic mechanical properties of the blends.