



CHAPTER I INTRODUCTION

Polymer blends are physical mixtures of structure different homo or copolymers. In the past decade, research into polymer blends has increased significantly. Blending has several sound economic advantages. Blending can generate a material with unique properties and/or processability, extend the performance of expensive resins, allow for the quick modification of performance, increase plant capabilities since most polymer blends are processed on standard processing equipment, be achieved through low capital investment, and be accomplished much more inexpensively than developing a totally new polymer.

An important case where the polymer-polymer mixture exhibits miscibility or solubility has provoked recent interest as miscible polymer blends are increasingly reported in the technical polymer literature. This is due to synergistic properties often result when components are truly miscible (in the thermodynamic sense), while partially or totally immiscible blends exhibit intermediate properties with the components. The formation of miscible blend requires the presence of favorable interaction between the component polymers. Two different polymers possessing complementary functional groups are likely to form a miscible blend. In this research, blends of ESCOR[®]310 terpolymers and Ethylene-acrylic acid (EAA) copolymers were studied. Both polymers contain acrylic acid groups, and it is thought that hydrogen-bonding interactions between these groups might lead to substantial miscibility. The techniques that were used are differential scanning calorimeter (DSC), dynamic mechanical analysis, thermal analysis, oscillatory rheological measurement, tensile measurements, hardness, gloss measurements, and X-ray diffraction measurement. It was apparented that a one-phase material with an extremely broad glass transition region near room temperature was obtained in this study and one possible application of this material is in sound and vibration dampening. The characteristic and miscibility of ESCOR[®]310/EAA blends were compared with that of previous work, which are ESCOR[®]320/EAA blends.

1.1 Basic Thermodynamic of Polymer Blends

In order for two polymers to be miscible, the Gibbs free energy of mixing must be negative. The expression that governs free energy of mixing is the familiar

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

The enthalpy term ΔH_{mix} is essentially independent of molecular weight and is a measure of the energy change associated with intermolecular interactions. It is the dominating factor determining miscibility of high molecular weight polymers. The entropy term ΔS_{mix} reflects the energy change associated with change in molecular arrangements. The magnitude of the entropy change is essentially an inverse function of the molecular weight, the lower the number of possible arrangements available to the segments of the covalently linked molecules.

The simplest system to consider is a mixture of nonpolar polymers. Because they are generally more attracted to themselves than to other polymers, ΔH_{mix} is usually positive. Assuming ΔH_{mix} is positive, $T\Delta S_{\text{mix}}$ must be greater than ΔH_{mix} in order for the Gibbs free energy of mixing ΔG_{mix} to be negative. However, because ΔS_{mix} is usually low for high molecular weight polymers, it is rarely sufficient to overcome the positive enthalpic contribution, and the Gibbs free energy of mixing is therefore positive. Thus, thermodynamics does not favor miscibility in nonpolar polymers than in blends of high molecular weight polymers.

When mixing polar polymers, the thermodynamic arguments are slightly different than those for mixing nonpolar polymers. Polar molecules may contain different functional groups, which attract each other upon blending. Consequently, the ΔH_{mix} for polar polymers may be negative, and since the entropy contribution is always negative, ΔG_{mix} can be negative. This satisfies the requirements for miscibility and explains why most miscible polymer blends comprise polar polymers. The specific interactions capable of inducing polymer miscibility include dipole-dipole interactions, ion-dipole interactions, hydrogen bonding, acid-base reactions, or charge transfer.

1.2 Determination of Polymer-Polymer Miscibility

Numerous techniques are used to determine if a polymer is single or multiphase.

1.2.1 Transparency

This method is easy and quick, but not totally reliable. 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.

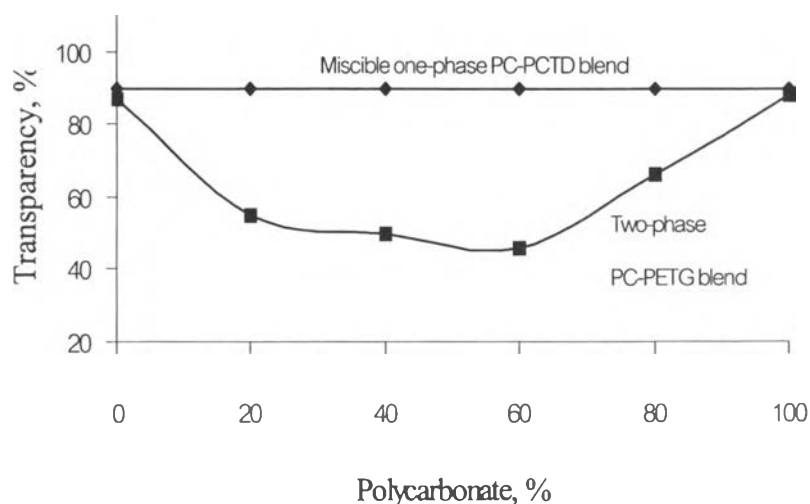


Figure 1.1 Transparency vs. composition for blends of PC with PCTD or PETG.

The transparency of a polycarbonate blend with two related polyesters is illustrated in Figure 1.1. Blends of PC with PCTD are transparent across the entire composition range, whereas blends of PC and PETG lose transparency at intermediate compositions. This suggests, but does not prove, that blends of polycarbonate with PCTD are miscible.

Erroneous conclusions may be reached with this method if the refractive indexes of polymer A and B are similar. The refractive indexes are essentially equal at room temperature, and blends are transparent even though they are two-phase.

Because the thermal coefficients of expansion of the individual polymers are different, the refractive indexes change upon heating or cooling to yield a mismatch, and transparency is lost. Furthermore, if the discontinuous domains are smaller than the wavelength of light, the light is not scattered, and a two-phase blend can be transparent. If either component of an initially transparent miscible blend later crystallizes, the blend of PC and PCTD when they are subjected to heat for extended period above the glass transition temperature of the blend. This allows the internal energy of the blend to be lowered because parts of the PCTD molecules are ordered into a crystalline phase.

1.2.2 Microscopy

It is a useful tool to determine if a blend is single or multiphase. Microscopy is the best applied to systems where the phases can be differentiated from one another by chemical or physical treatment such as staining or solvent swelling.

1.2.3 Glass-Transition Temperature

The Glass-transition temperature 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 a polymer blend. For example, a miscible one-phase blend should have only one T_g , whereas a two-phase blend should have two glass transition, one for each phase. The T_g is usually determined by differential scanning calorimetry (DSC). With miscible one-phase blends, only one T_g is observed at a temperature, which lies between that of the pure polymers.

1.2.4 Other Techniques

In addition to the more common approaches of microscopy and calorimetry, a variety of experimental techniques have been used to determine the miscibility of polymer blends. These techniques include thermomechanical, dynamic mechanical, thermoelectrical, and dilometric procedures. Most of these are based on the determination of the number and location of the glass-transition temperatures.

Still other techniques such as light, X-ray, and neutron scattering or NMR provide much insight into the blend morphology.

1.3 Rheological Measurement

All materials behave in a viscous or elastic manner that depends on how quickly or slowly they are deformed. This led to a new word viscoelasticity. In other words, the mechanical properties of material are time dependent. Time-dependent mechanical property measurements are important for the characterization of polymers, particularly to determine their response under conditions of processing or use. Both the elastic and viscous or damping characteristics can be obtained from this measurement. Elastic materials store energy; that is, they convert mechanical work into potential energy, which is recoverable. Viscous or damping behavior causes the deformation to be out of phase with the stress applied.

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

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

The dynamic modulus can also be resolved into two components:

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

where

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

and

$$G' = |G^*| \cos \delta$$

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

where G' = storage modulus and G'' = loss modulus

The loss modulus G'' arises from the out-of-phase components of τ^* and γ^* and is associated with viscous energy dissipation, i.e damping. The ratio of G'' and G' gives another measure of damping called the dissipation factor or loss tangent.

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

1.4 Dynamic Mechanical Measurement

Dynamic Mechanical Properties are the mechanical properties of materials as they are deformed under periodic forces. The dynamic modulus, the loss modulus, and a mechanical damping or internal friction or $\tan \delta$ express these properties. The dynamic modulus indicates the inherent stiffness of material under dynamic loading conditions. Shear, tensile, or flexural modulus is determined as a function of temperature and frequency or time.

The investigation of the dynamic modulus and $\tan \delta$ over a wide range of temperature 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, degree of crystallinity, molecular orientation, cross-linking, phase separation, structural or morphological changes resulting from processing, and chemical composition of polymer blends, graft polymers and copolymers.

Typical dynamic mechanical properties of polymers as a function of temperature are illustrated in Figure 1.2.

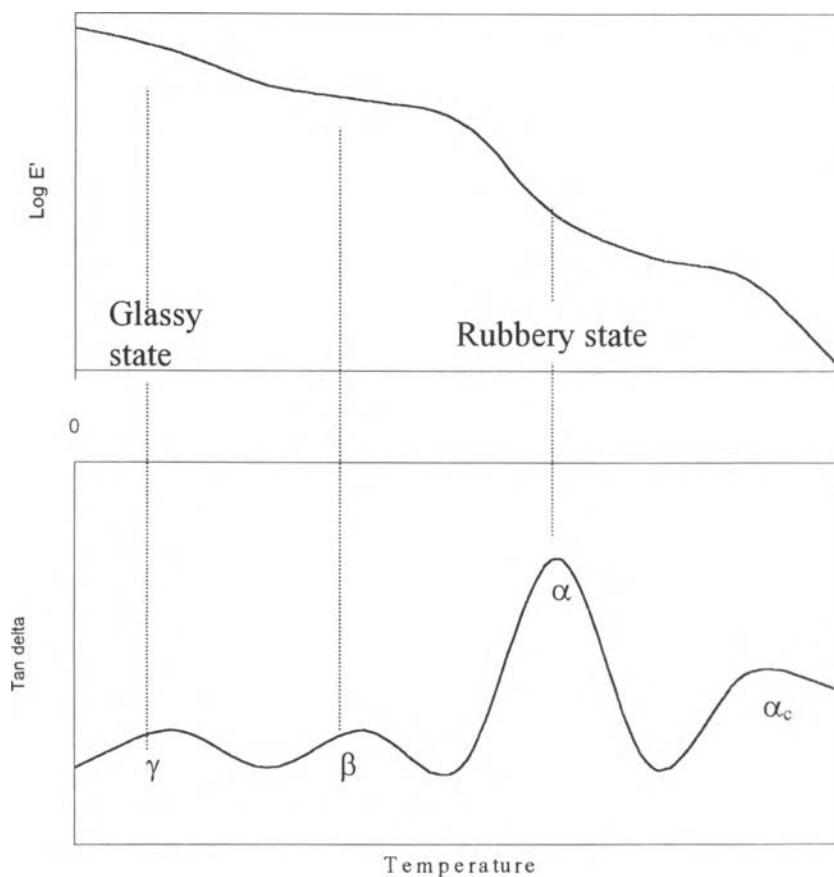


Figure 1.2 Typical dynamic mechanical properties of polymers.

The primary relaxation of a crystalline polymer (α -peak), corresponding to the glass transition (T_g), resulting from the initiation of micro-brownian motion of the amorphous chains. In this glass-transition region, the dynamic modulus of the glassy state decreases to leathery-state around 100 times the modulus in rubbery state. The appearance of the leathery state is caused by the micro-brownian motion of the noncrystalline region under the structural restraint of the neighboring molecular chains in the crystalline region. For this reason, even after crystallizing a given polymer, the α -peak tends to shift to higher temperature and broaden in comparison with the amorphous state.

Highly crystalline polymers, such as HDPE, exhibit another dispersion between the α -dispersion and melting temperatures. This relaxation, called the α_c -

or α -dispersion, has been attributed to molecular motion within the crystalline phase. This crystalline dispersion is due to the friction viscosity among specific crystalline planes or molecules inside the crystals.

Other relaxation transitions can be found in a glassy state on the lower temperature side of the primary dispersion. These are called secondary dispersions and are usually designated β , γ , in order of decreasing temperature. The β -dispersion is associated with motion about the chain backbone of a relatively small number of monomer units or with motion of side groups. The γ -dispersion can be related to the side-group motions in the amorphous and crystalline phases, end-group rotation, crystalline defects, backbone-chain motions of short segments or groups, and phase separation of impurities or diluents.

1.5 Vibration Dampening

Structural dampening refers to the capacity of a structure or structural component to dissipate energy or to its capacity for removing from the structural vibration some of the energy associated with that vibration. This removed energy may be converted directly into heat and transferred to connected structures or to the ambient media. It has been known that by utilizing layers of viscoelastic shear dampening material, the dissipation of energy within the vibration members themselves can reduce noise and vibration levels. A combination of viscoelastic dampening material and metal called laminated steel sheet will provide strength and rigidity but with a low response to vibration. The basic structure of the vibration dampening laminated steel sheet is shown in Figure 1.3.

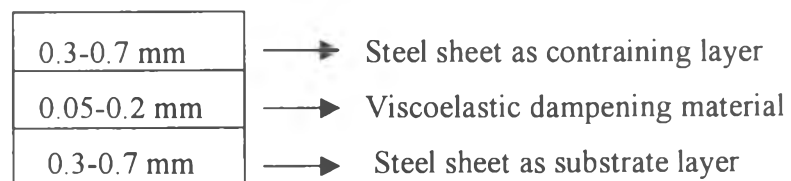


Figure 1.3 The basic structure of the vibration dampening laminated steel sheet.

Since the important quantities of viscoelastic materials under dynamic load environments are the storage modulus E' and the loss modulus η , the effects on these quantities are temperature, frequency, cyclic strain amplitude, and static preload.