

CHAPTER I

INTRODUCTION.

INTRODUCTION

There has been much awareness regarding the harmful effects of polymer materials on the environment. Conventional non-degradable polymer systems (e.g. polyethylene, polypropylene etc.) are used for high volume, short-term applications such as packaging, medical, automobile and agricultural areas. These synthetic polymers cannot be degraded easily after their life cycle has been completed and so a portion of this volume ultimately litters the environment. Recycling is obviously a better choice at a higher cost but most countries cannot afford to recycle all its polymer wastes. Moreover, all polymers are not recyclable since their properties after recycling are poor compared to their original ones and they are of less economic value. This leads to the quest for new as well as modified degradable polymers, which can replace existing synthetic polymers. Replacement of these polymer systems requires that the degradable polymers have properties that are sufficiently comparable to those of the conventional polymers. These desirable properties can be achieved by creating new environmentally friendly polymers or modifying existing degradable polymers. The term '*degradable polymers*' relates to the polymeric materials that disintegrate under environmental conditions in a reasonable and demonstrable period of time [Narayan (1990)]. Degradation of polymers may occur by any of the following mechanisms [Swift (1990)].

Biodegradation : It is promoted by enzymes and may be either aerobic or anaerobic and provides for complete removal of the polymer from the environment.

Photodegradation : It is promoted by irradiation, e.g. sunlight, and it rarely leads to complete removal, though small fragments may be produced for subsequent biodegradation.

Environmental Erosion : This is promoted by weather elements such as wind, rain, temperature and larger animals. This also cannot remove the polymer completely.

Chemical Degradation : This is promoted by the chemical reactions through additives, e.g. metals and functional groups, which produces smaller fragments of the polymer.

However, any or all of the above mechanisms may be operative on any degradable polymer, with complete removal from the environment being the ultimate goal which can only be achieved by biodegradation.

BIODEGRADABLE POLYMER

The biodegradation of polymers proceeds by hydrolysis and oxidation. The presence of hydrolysable and/or oxidizable linkages in the polymer main chain, the presence of suitable substituents, correct stereoconfiguration, balance of hydrophobicity and hydrophilicity, and conformational flexibility contribute to the biodegradability of the polymers [Huang et.al. (1995)]. Biodegradable polymers may be divided into three classes : (a) natural polymers originating from plant or animal resources (e.g. cellulose,

starch, protein, collagen, etc.), (b) biosynthetic polymers produced by fermentation processes by micro-organisms (e.g. poly-hydroxy alkanates), (c) certain synthetic polymers possessing the biodegradable properties explained earlier (e.g. polycaprolactone and poly-lactic acid).

Natural polymers like cellulose and starch are not thermally processable unless modified. Cellulose has a degradation temperature below its melting temperature and hence cannot be processed in the melt. Moreover, because of its complex morphology of crystalline regions and hydrogen bonding, cellulose is difficult to dissolve in common solvents. Processing with the help of a suitable solvent has been possible with N-methylmorpholine N-oxide (N-MMNO) and water [Chanzy et.al.(1980)] or dimethylacetamide (DMAc)/lithium chloride (LiCl) [Turbak et.al. (1982)]. Hence cellulose can be spun into lyotropic liquid crystalline fibers [Dave and Glasser (1993)], but the process is complicated and dangerous due to rigorous solvent handling protocols. However, modified cellulose, such as cellulose esters, can be melt processed as a thermoplastic polymer, since their melting temperature can be significantly reduced below their degradation point [Sealey et.al (1996)]. Similarly, modified starch has been incorporated into polymer blend systems to provide biodegradability [Maddever (1990)].

On the other side, poly (hydroxy alkanates) (PHA) are high molecular weight polymers produced by bacteria or other microorganisms. A variety of PHA's can be synthesized by bacteria depending on the species of bacterium and the compounds supplied as carbon sources for growth. PHA's are biodegradable and biocompatible thermoplastics which can be melted and molded [Gilmore et.al. (1990)]. These polymers have attracted attention because of their potential use in both medical and industrial applications owing to the properties of biocompatibility and biodegradability.

The other group of biodegradable polymers that has been of interest includes the synthetic polymers like poly-lactic acids and polycaprolactone. However, in case of these polymers, morphology affects the degradation process [Jarret et.al. (1981)]. Amorphous regions are preferentially degraded first due to their greater surface area compared to the spherulites. Similar effect of morphology on degradation has been observed in case of more crystalline poly (alpha-hydroxy acids). However, varying the stereoisomer ratio of D- or L-lactate units, poly (lactic acid) can be made semicrystalline or fully amorphous [Christel et.al. (1982)].

LIGNIN

Lignin is an amorphous, aromatic biopolymer second in natural abundance only to cellulose and is obtained from almost all types of natural wood based resources [Glasser and Kelley (1987)]. It is a byproduct of pulp and paper mills and is conventionally treated as a waste material having low economical usage. It is separated from the cellulose conventionally either by strong alkaline or acidic solutions, or by a high pressure steam treatment followed by solvent extraction. Unmodified lignin often possesses poor solubility and thermoplastic melt flow characteristics like cellulose. Similar to thermoplastic cellulose ester derivatives, one method adopted for improving the properties and use of lignin as a thermoplastic polymer is by esterification. Esterifications of lignin have been in practice from the late forties when it was found to be useful as a mold lubricant and possessing characteristics of softening point and solubility [Lewis and

Brauns (1947)]. More studies were carried out by Glasser and Jain on unmodified and bleached lignin esters [Glasser and Jain (1993)]. Enhanced solubility and melt characteristics along with a reduction in glass transition temperature and improved thermal decomposition behavior were reported for lignin alkanoates. However, lignin and its derivatives are biodegradable and can be effectively utilized in combination with other biodegradable polymers. A high degree of phase mixing was reported for the continuous fibers prepared from anisotropic solutions of cellulose acetate butyrate and lignin in DMAc [Dave and Glasser (1997)]. Moreover, the incorporation of lignin in CAB decreased the dynamic viscosity, dynamic elastic modulus and dynamic loss modulus. This predicts some form of compatibility of lignin and its derivatives with other biodegradable polymers like cellulose acetate butyrate (CAB). Lignin has a higher modulus than CAB and so acts as a modulus builder. Use of lignin as a modifier of some biopolymers would certainly be advantageous in the sense of its utilization as well as recovery of biomass.

POLYMER BLEND

Along with the ongoing search for new materials, modifications of existing polymers by blending have shown directions in economically tailoring materials so as to have desirable properties. The phenomenon of mixing, or blending of two materials has been known to mankind from prehistoric ages when new metal alloys like bronze was discovered. Ideally, two or more polymers may be blended together to form products that show desirable combinations of properties. But this ideality is seldom attained due to some inherent and fundamental problems. Most of the polymer pairs are not thermodynamically miscible and so exist in two different phases in the polymer blend. This breakdown into two phases creates an interface, which might lead to poor performance of the blend system. A typical case of high interfacial tension and poor adhesion between the two phases leads to lower degree of dispersion and gross separation during later processing or use. Poor adhesion also produces very weak and brittle mechanical properties due to poor stress transfer between phases and hinders the formation of highly structured morphologies [Paul, 1978].

Polymer multi-component systems can be categorized into a) polymer blends, b) copolymers and c) reinforced composites. Our discussion here is mainly related to the polymer blend systems in which the polymers are not connected to each other by chemical bonds as in case of copolymers. However, better dispersion can be expected in case of a copolymer than that of a blend system consisting of same polymer pairs. Still it has been observed that nearly all copolymers exhibit some degree of phase separation [Kollinsky, 1971]. Thus to define the interaction between the polymer pairs at the molecular level, the term “compatibility” has been used in technological literature. Compatibility is not synonymous with miscibility since it is used to characterize the relative ease of fabrication or performance of the two polymers in a blend. Blend components which can resist gross phase segregation and/or show desirable blend properties are frequently said to possess some degree of compatibility though they may not be miscible at all from a thermodynamic point of view [Paul, 1978].

COMPATIBILITY

The term compatibility has been used to describe complete mixing at molecular level. But when it comes to macromolecules or polymers, the molecular dimensions can be large enough to describe the significance of the term “compatibility”. Many heterogeneous systems can be defined as compatible by this definition though they show a large degree of phase separation and two distinct glass transitions. Thus the compatibility or homogeneity of a polymer blend can only be defined in relative terms of dimensions of the separate phases which can generally be characterized by different measurement techniques such as Differential Scanning Calorimetry (DSC), Dynamic Mechanical Spectra (DMS), Thermo-Mechanical Analysis (TMA), Nuclear Magnetic Resonance (NMR) etc.

Hence, compatibility is treated as a relative term and can be defined by a compatibility number, [Kaplan, 1976]

$$N_c = \frac{\text{Experimental Probe Size}}{\text{Domain Sizes of Phases}}$$

The experimental probe size can be taken as the scale of resolution of an instrumental technique. The domain size is the average dimension of the dispersed phase in the polymer blend.

Thus, i) when $N_c \longrightarrow \infty$, the system is compatible
 ii) when $N_c \longrightarrow 1$, the system is semicompatible
 iii) when $N_c \longrightarrow 0$, the system is incompatible

Figure 1.1 is a schematic representation of a two phase system which illustrates the definition of a compatible, incompatible and semicompatible system by using DMS. When N_c approaches zero, the dimension of each existing phase is much greater than the probe size of the instrument and so the instrument can detect two transitions corresponding to each phase component. Here two distinct T_g 's are observed.

For the compatible case (i.e., N_c approaches ∞), the probe size is much greater than the phase dimensions and so the instrument is unable to detect small compositional fluctuations and so report a single T_g which is an average of the contributions of each component.

For the semicompatible case, a broader effect is found and the $\tan \delta$ curve shows a great deal of damping over the entire temperature range from the lower to the higher transitions associated with each component.

Therefore, the detection of a single or double transition in a two phase system by an DMS-instrument gives an indication of the dimensions of the phases present in the system. The dimension that corresponds to a dynamic mechanical thermal analysis is approximately 15 nm [Kaplan, 1976]. NMR technique on the other hand can detect composition fluctuations in the dimensional range of 2.5-5 nm [Masson and Manley, 1992].

POLYMERIC PLASTICIZER

A plasticizer can be defined as a chemical which reduces the stiffness of an amorphous (glassy) thermoplastic resin [Hammer, 1978] whereas an antiplasticizer conversely increases the stiffness. The fundamental principle associated with a plasticizer is to interact with the polymer chains on the molecular level so as to speed up the viscoelastic response of the polymer. Thus it actually increases the molecular mobility of the polymer chains and consequently this decreases the glass transition temperature (T_g) of the polymer. Moreover, a plasticizer may influence the processability of the polymer as well. In case of a low- T_g polymer (having more or less flexible chains), both effects (i.e. lowering of stiffness as well as improving processability) can be observed. On the other hand, if the polymer has a high T_g , and a high melt viscosity, dramatic improvement in processability is observed without much change in polymer chain stiffness.

The conditions required of a polymeric plasticizer are : [Hammer, 1978]

- a) Must be compatible on a molecular scale with the polymer to be plasticized.
- b) Must have a sufficiently low T_g so that it will efficiently lower the T_g of the polymer to be plasticized.
- c) Have sufficiently high molecular weight to justify the term “polymeric” (versus oligomeric). (approximately $M_n \geq 5000$). Also this implies the permanence requirements, which relates to low vapor pressure and low diffusion rate, of the plasticizer within the polymer.

Although these are the required conditions, in the strict sense of the term, the polymer with a lower T_g can be called a polymeric plasticizer for the polymer with a higher T_g in a compatible blend system. If the polymer to be plasticized is semicrystalline, a plasticizer would subsequently depress the melting temperature and also reduce the degree of crystallinity in most cases (note that cases where the plasticizer acts as a nucleating agent are not considered). The plasticizer forms a compatible blend with the polymer in the amorphous phase whereas very little actually goes into the crystalline phase. Thus, a two phase system is obtained after the addition of a compatible additive – one phase being composed of pure crystalline polymer and the other being a compatible amorphous blend. In spite of the fact that the blend system has two separate phases varying in composition, it can be called “compatible” since the molten blend forms a homogeneous mass at temperatures above the crystalline melting point of the polymer. However, if the crystallinity is well developed, it is difficult to find a plasticizer sufficiently compatible with (soluble in) the polymer to have a significant effect on its properties. The efficiency of a plasticizer can be evaluated by various semi-empirical parameters such as dilution ratio, dilute solution viscosity of the polymer in the plasticizer, depression of the glass transition temperature, melt viscosity of the plasticized polymer, electrical or mechanical properties, or the molecular size or shape of the plasticizer itself [Billmeyer (1994)].

OBJECTIVES

This study is based on modifying (by blending with lignin derivatives) some biodegradable polymers which have been (or may be in the near future) commercialized as biodegradable plastics. The polymers considered here are cellulose ester (cellulose acetate butyrate) (CAB), thermoplastic starch-caprolactone blend (SCL), and polyhydroxy alkanates (PHB and PHBV). These polymers have attracted considerable interest as promising materials having good bio-compatibility and environmental degradability. But some of these polymers do lack the mechanical properties, such as toughness (e.g. polycaprolactone) and ductility (e.g. polyhydroxy-alkanoates), and some are badly affected by heat due to rather low melting transitions (e.g. polycaprolactones) or decomposition temperatures (e.g. polyhydroxy-alkanoates). These undesirable properties may be prevented by modification of these polymers by blending with a low molecular weight biopolymer (lignin) and its derivatives. However, compatibility of the lignin and lignin derivatives with the other components has to be established before it can be used for applications in blends with other thermoplastic polymers. The effect of lignin and lignin derivatives on these biodegradable polymers (CAB, PHB, PHBV and SCL) will be covered in this thesis. Compatibility studies along with some morphological and mechanical properties will be dealt with for these biodegradable blends.

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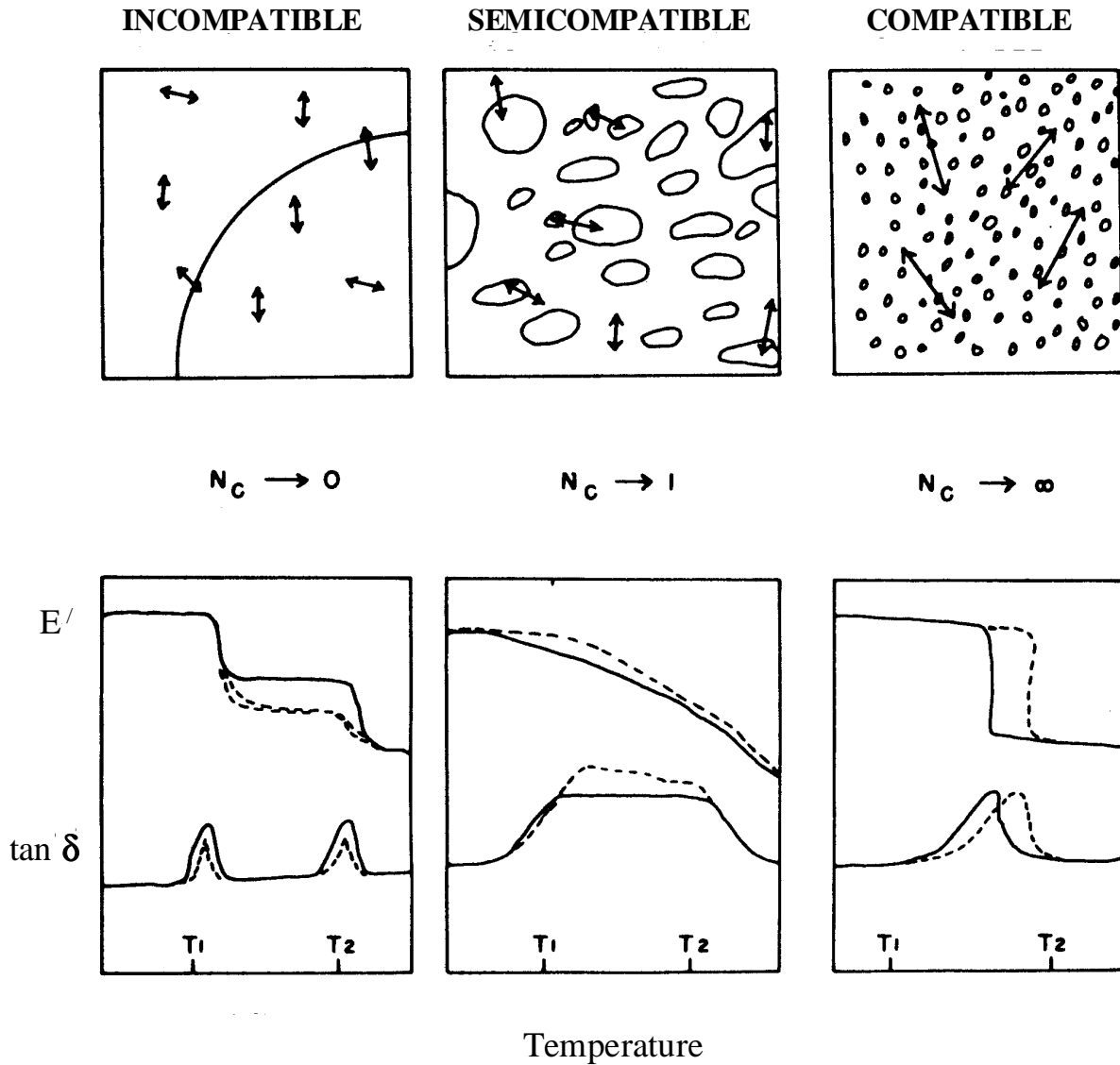


Figure 1.1 : Schematic diagram of electron micrographs of two-phase systems and the corresponding dynamic mechanical spectra below. Arrows represent probe size. [Reproduced from Kaplan, 1976].