

CHAPTER I

INTRODUCTION

To develop new polymeric materials for both scientific and commercial progress, polymer blending is the combination of two or more than two kinds of amorphous polymers to get the excellent properties of each component. Blending process usually carried out in molten state or in solution state because in these states each polymer component will have more chance to contact and mix together. At equilibrium, a mixture of two amorphous polymers may exist as a single phase mixed segments of two macromolecular components at molecularly mixed level called miscible or compatible blending. In the other case it may separate into two distinct phases consisting primarily of the individual components which cannot be mixed or dissolved each other called immiscible or incompatible blending. An incompatible blend can be converted to a compatible blend by adding a compatibilizer, chemicals or additives which is added into polymer blend to help mixing by exhibiting interfacial attractions in between separate phase of immiscible blend.

Low density polyethylene (LDPE) is a general purpose plastic, which is a polyethylene contains alkyl substituents, or short-chain branches on the chain backbone. The density of LDPE is 0.912-0.935 g./cm³ and T_m is 105-115°C. LDPE is a chemical resistance material especially to polar compound and low permeability to water and many aqueous solutions. LDPE is tough and highly ductile over a wide temperature range.

Nylon is an important engineering plastic, which contains amide group in the main chain. Nylon uses are various depend on the various types of nylon, the properties and the additive adding in the process. Nylon 6 has various properties such as good melt flow, easy to process, water sensitive, high rigidity, weather and thermally resistant and good barrier properties. T_m of nylon 6 is 228°C.

In this research, nylon and LDPE will be blended together. However, there are some previous studies shown that nylon and LDPE blend (*P.M. Subramanian, 1985*) gave incompatible blend because the structure of LDPE and nylon have very different polarity. LDPE contains only nonpolar ethylene groups but nylon contains partially polar amide groups in the polymer chains. Ionomer, Surlyn, the polymer contain both LDPE, which is nonpolar part, copolymerized with methacrylic acid, which is polar part, will be introduced to combine the two components together. In blending of these two polymers compatibilily, the excellent properties of two polymers can be obtained effectively and the production cost can be reduced.

1.1 Theoretical Background

1.1.1 Low Density Polyethylene (LDPE)

Low density polyethylene (LDPE) is a polyethylene which contains alkyl substituents, or short-chain branches on the chain backbone. The branches of LDPE contain 2-8 carbon atoms. The unit cell of LDPE in the crystalline phase is orthorhombic, and contains four ethylene units. The polyethylene (PE) chain is in linear zigzag form, with a repeating unit of only one ethylene unit. The short-chain branches present in high pressure polyethylene disrupt chain-folding and reduce crystallinity to 40-60 %, T_m to 105-115 °C and density to 0.912-0.935 g/cm³. The important properties for blending process, which have to be concerned are chemical, physical and rheological properties. In chemical properties, LDPE is chemical resistance material especially to polar compounds due to its molecular structure contains only non-polar molecules. LDPE is low permeability to water and many aqueous solutions. It can be slowly attacked by some chemicals such as oxidizing agents, aliphatics, aromatics, and chlorinated solvents. These chemicals will make LDPE swollen at room temperature, and LDPE can be dissolved after temperature is raised. Some chemicals such as nitrogen, oxygen, and carbon dioxide can pass through LDPE film but poly(vinylidene chloride) and polyamide. In physical properties, both stiffness and yield strength depend on temperature and crystallinity, as indicated by density. At ambient temperature, stiffness increases logarithmically as density increases from 0.910-0.950 g/cm³. At higher temperatures, the stiffness drops very sharply. At normal usage temperature, the yield strength is not strongly dependent on straining rate because of the high ductility, but become more dependent as temperature decreases. LDPE is highly ductile over a wide temperature range. It is not used in continuous application of high stress required because of creep and stress relaxation occurs slowly. Both properties

will induce LDPE to be slowly deform under constant stress. LDPE is tough. It exhibits good impact strength over a wide temperature range because failures are of the ductile type except at extremely low temperature. LDPE typically have brittle temperature below $-70\text{ }^{\circ}\text{C}$; values as low as $-118\text{ }^{\circ}\text{C}$. Variations in cooling rates also resulted in differences. Sample imperfection increases the brittle temperature. Transition temperature usually decreases with increasing molecular weight and branching. Degree of crystallinity and spherulitic structure depends on thermal history. Thermal aging increases spherulite size, which normally increases brittle temperature. The tensile stress substantially lower than those short time rupture will make LDPE has stresscracking over long periods up to many years. In rheological properties, polyethylene undergoes shear-thinning behavior. The molten state PE may be classified as a pseudoplastic material and its viscosity decreases with increasing shear stress. Molten PE exhibits elastic properties over a wide temperature range, such as die swell and elastic recovery when stress is removed. At low shear rates, die swell increases as molecular weight, long chain branching and shear rate increase. Melt fracture depends on the length of branches.

1.1.2 Polyamide (nylon)

Nylon is an engineering plastic resins, which has polyamide structures as shown below.

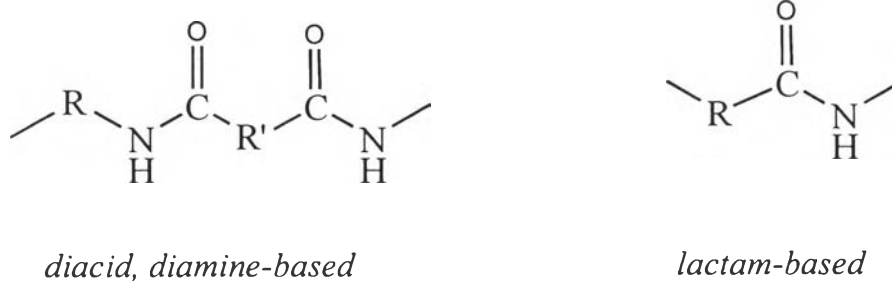


Fig 1.1 The repeating unit of polyamide (nylon)

Nylons can be classified as either semi-crystalline or amorphous polymers. Each kind of nylon has different properties, which are suitable for different usages. The semi-crystalline nylons are white, chemically and hydrolytically stable. The flammability increases with aliphatic carbon increase. Some physical properties of semi-crystalline nylon can be improved by adding some fillers, such as mineral- and glass-filled which can impart creep resistant properties to nylon. Nylon has good melt flow and rapid crystallization rate making it easy to process. Amorphous nylon resins are more difficult to process than semi-crystalline nylon resins because they can have lower heat-deflection temperatures and stiffer melt flow than filled semi-crystalline nylon resins. However, amorphous nylon resins have less problems than semi-crystalline nylon resins because warpage is reduced and dimension stability are excellent. Nylons have various properties, which are effected from various structures and additives added. For example, nylons are water sensitive polymers due to the hydrogen bonding character of the amide group. The amount of water depends on the amide groups, which present in polymer chain. Water absorption decreases with decreasing amide groups concentration in polymer backbone. Water can acts as a plasticizer, which reduces tensile strength and modulus while increasing elongation at break and consequently toughness. Nylons are also high rigidity, weather and thermally resistant and good barrier properties.

1.1.3 Ionomer

Ionomer is the generic term for polymers containing interchain ionic bonding. These ionic crosslinks occur randomly between the long chain polymer molecules to produce solid state properties usually associated with high molecular weight. This is mean that ionomers or ionic polymers are the polymers which contain pendant salt groups attached to the polymer chains. The pendant salt groups of ionomers make the polymer higher polarity. The

combination of low content and low polarity backbone results in a class of commercial polymers, which continue to be scientific interest. The pendant ionic groups interact to form ion-rich aggregates contained in the nonpolar polymer matrix. The resulting ionic interactions strongly influence polymer properties and applications. The ionic interactions and resultant polymer properties are dependent on the type of polymer backbone; ionic functionality (ionic content), 0-10 %; type of ionic moiety (carboxylate, sulfonate, or phosphonate); degree of neutralization (0-100 %); and type of cation (amine, metal, monovalent, or multivalent). A common commercial ionomer is Surlyn A[®], a copolymer of ethylene and about 15 % of methacrylic acid. About 33 % of the methacrylic acid comonomers are neutralized with sodium hydroxide to produce the sodium salt. Ionic bonding provides a tough material Poly(ethylene-co-methacrylic acid)s introduced by Du Pont in 1964 were the first ionomers whose physical properties were recognized as a consequence of phase-separated ionic-rich domains. The number of ionic groups existing in clusters is strongly dependent on polarity of the polymer matrix, only multiplets are favored, whereas with increasing ionic content, cluster formation is favored. Although Poly(ethylene-co-methacrylic acid) ionomers has low concentrations of methacrylic acid into the ethylene backbone has little effect on properties, the neutralization of these group are more drastically influence. Bulk poly(ethylene-co-methacrylic acid)s are neutralized on two-roll mill at 150-200 °C by addition of aqueous sodium hydroxide or other bases in water to the fluxed copolymer. As the water evaporates, the melt viscosity increases markedly, and when sufficiently neutralized, the ionomer can be stripped off the mill in the shape of a tough, flexible sheet.

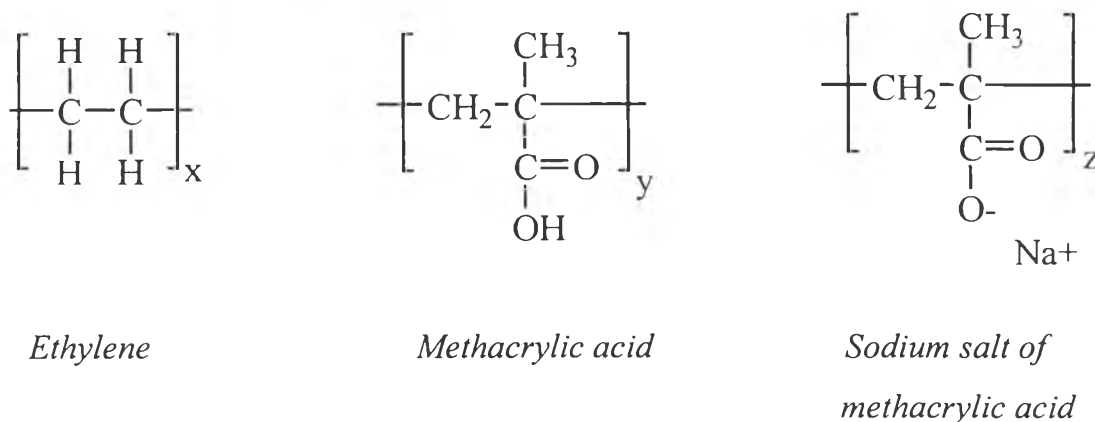


Fig 1.2 The structure of comonomer units in Surlyn A[®]

The acid groups promote excellent adhesion to various substrates and increase abrasion resistance, but impart corrosivity. Toughness and flexiness are outstanding and are maintained at low temperatures. Puncture and impact resistance are the other toughness characteristics of material. Stress crack resistance increases with increasing carboxyl content. Optical clarity is good. Electrical insulation properties are characteristic of zinc ionomers. They have good dielectric properties over a broad frequency range. Because of ionic bonding, sodium or zinc salts of methacrylic acid copolymers exhibit properties similar to those LDPE of high molecular weight. Ionomers contain polar groups, which relate to the solubility and adhesion. Glass reinforcement increases heat and creep resistance significantly. Adhesion to aluminium foil and metal is another characteristic related to carboxyl content. Most commercial ionomers comply with FDA regulations for food contact.

1.1.4 Polymer Blending

To blend two polymers together, there are two methods for preparing blends. These are melt mixing and solution casting. In melt mixing, care must be taken in some condensation-type polymers, interchange reaction

may occur during melt mixing giving a copolymer; a single-phase structure can be resulted which may give the impression that the two polymers are physically miscible when they may not be. In solution methods, often used for small quantities or for polymers not amenable to melt processing, offer other opportunities for misleading result. Blending two polymers can result in two different behaviors. These are immiscible blend and miscible blend. In immiscible blend, there is phase separation causes light scattering or limited transparency. However, since the domains may be small relative to the wavelength of light or have similar refractive indexes, thus limiting the extent of light scattering. Conversely, a miscible blending, a blend with a miscible amorphous phase may also contain a crystalline phase, which scatters light and reduces transparency. The simple methods usually use to determine which blend is miscible blend or immiscible blend is the glass-transition behavior of a polymer blend and it is examined by the thermal, mechanical, dielectric, or similar techniques. For miscible blend, it will show a single, composition-dependent glass-transition, reflecting the mixed environment of the blend, and for immiscible blend, it will show two t_g s characteristic of each phase.