CHAPTER I

INTRODUCTION

1.1 Engineering thermoplastics

Reprocessing is carried out extensively in the plastic industry. It is interesting mainly for economic and environmental reasons. Reprocessing may give rise to deterioration of properties due to thermal, thermooxidative, or mechanical degradation. Engineering thermoplastics are widely used in many fields because of their good properties.

Engineering or high performance plastics have good mechanical properties, excellent resistance to thermal degradation, and chemical attack which allows them to compete with metals in low to medium temperatures [JEAN-MICHEL, 1991; A.A COLLYER, 1994].

1.1.1 Nylon 6,6

Nylons are polymers characterized by an amide group (-CONH-) in the main polymer chain. The aliphatic polyamides, or nylons, were the first materials to be recognized as engineering thermoplastics, owing to their superior mechanical properties, especially when exposed to elevated temperatures or solvents. These properties allowed polyamides to be used in applications previously satisfied only by metals [MARGOLIS, 1985].

Nylon 6,6 is prepared from hexamethylene diamine and adipic acid. It is a semicrystalline thermoplastic. It has a high melting temperature (T_m) of 265 °C compared with 135 °C for polyethylene, and this large difference has been attributed to forces between the polar groups in the molecules. Interchain hydrogen bonds between the C=O groups of one molecule and the N-H groups of the adjacent chain have been demonstrated. But once the inter-molecular forces have been overcome, the flexible methylene groups between the stiff amide group give rise to low melt viscosity [BABANIYI and DAVID, 1992].



Figure 1.1 The chemical structure of nylon 6,6.

Nylons generally have a high affinity for water, and their physical and mechanical properties are often significantly affected by the absorption of moisture. The hydrogen bonded chain and links in the disordered region that from a crosslinked network are broken easily by a number of different environmental effects such as moisture absorption, high temperature and stress [BABANIYI and DAVID, 1992]. Nylon 6,6 is susceptible to surface oxidation in air at elevated temperatures with an accompanying loss of mechanical properties. This oxidation reaction is not important in many applications but limits applications that involve long exposures at temperature above about 75-85 °C [MARGOLIS, 1985]. The first stage involve oxidation of the amine end group.

OOH

Hydroperoxide I

This hydroperoxide then decomposes by chain scission to a variety of products including CO₂, ammonia, and some cyclopentane [STEPPEN and DOHERTY, 1991]. This results in lower molecular weight and loss of mechanical properties [MARGOLIS, 1985].

Nylons are used in many fields such as electrical and electronics, industrial and machinery, monofilament, film and coatings.

1.1.2 Polyoxymethylene (POM, Polyacetal, Acetal)

Polyoxymethylene (Polyacetal) is an engineering material competitive with nylons, metal and ceramics. The first commercially available Polyacetal was marketed by Du Pont in 1959 under the trade name Delrin [MARGOLIS, 1985]. -(CH₂-O)_n-

Figure 1.2 The chemical structure of polyoxymethylene.

Because of the symmetry of the repeat unit, the melting temperature of Polyacetal is relatively high (180 °C) and methylene and oxygen linkages in the chain give flexibility in the melt. This gives good processability [A.A COLLYER, 1994].

Polyacetal molecules have a short backbone (-C-O-) bond which permits close packing, allowing a degree of crystallinity of at least 70 % [JEAN-MICHEL, 1991]. The dense structure accounts for the resin's high density and it offers high mechanical strength, stiffness, toughness, and practical impact strength through broad ranges of temperature and environment. Physical and mechanical properties are dependent upon the degree of crystallinity [MEDELLIN and PHILLIPS, 1990 ; MARGOLIS, 1985]. Polyacetals have the following characteristics :

- 1. High tensile strength, shear strength, stiffness, and toughness.
- 2. Predictable stress/strain relationships
- 3. Predictable dimensional behavior.
- 4. Chemical and corrosion resistance
- 5. Abrasion resistance
- 6. Light weight
- 7. Acceptability for food contact applications (most grades)
- 8. Ease of processing
- 9. Competitive costs

Polyacetal can decompose with the formation of toxic formaldehyde gas if overheated during the melting process. End group encapping is essential, otherwise depolymerization ("unzipping") would occur under molding conditions. The capping of the end group can be achieved by etherification, or esterification [ULRICH, 1993]. The unziping reaction is a rapid sequence of chemical reaction steps progressing along a polymer chain. A polymer degradation reaction which is particularly important is the loss of monomer molecules by depolymerization [UHELAN, 1994]. The commercial polyacetal (Delrin) has hydroxyl end groups that are acetylated to prevent depolymerization by an unziping reaction that occur at 127 °C [A.A COLLYER, 1994].

Although in many respects polyacetal resins are similar to nylons, they are superior in their fatigue endurance, creep resistance, stiffness and water resistance. The nylons (except under dry conditions) are superior in impact toughness and abrasion resistance [BRYDSON, 1982].

Polyacetals have found and are continuing to find widespread usage in the automotive, industrial, pumbling, appliance and other fields [MARGOLIS, 1985]. Over 80% of the applications involve the replacement of zinc, steel, aluminum, and brass [A.A COLLYER, 1994].

1.1.3 Polyetherimide (PEI)

Polyimides are among the most temperature resistant engineering plastics.



Figure 1.3 The chemical structure of polyetherimide.

Polyetherimide (PEI) comprises two ether linkage (-O-) and contributes enough flexibility to the chain give it good melt processability and flow. The amorphous character of the resin gives it good dimensional stability and inherent transparency [JEAN-MICHEL, 1991]. The aromatic imide provides stiffness, rigidity, creep resistance, and a high heatdeflection temperature. PEIs have 3 important characteristics [MARGOLIS, 1985];

- 1. Outstanding melt flow for a high-heat material.
- Melt stability which provides a processing window of over 82 °C with no degradation.
- 3. The ability to be moulded using conventional polymer processes.

PEIs exhibit high strength and high modulus, good ductility, excellent thermal stability and flame resistance. The above basic properties make PEIs outstanding high performance engineering thermoplastics [WILSON et.al., 1990].

Present applications of PEI are found in the electronic area such as for transparent parts (fiber optic connectors), in air craft engine components, and in high intensity lighting systems. Thin films can be made which have very good dimensional stability [JEAN-MICHEL, 1991].

1.2 Mechanical properties

The basic characteristics of the mechanical properties of solids are usually determined by tests resulting in variations deformation-vs.-stress dependencies, such as stress-strain diagrams. Examination of such dependencies readily brings out characteristics of elasticity, plasticity, and strength [ROSATO, 1993].

These include both destructive and non-destructive tests. The destructive tests may include tensile, compression or shear testing, and other product-related tests such as tear, abrasion, flexural and impact testing. Non-destructive tests may vary from simple visual examination and weight, density or hardness tests [HUNT and JAMES, 1993].

1.2.1 Tensile strength

The tensile test is the experimental stress-strain test method most widely employed to characterize the mechanical properties of materials like plastics, metals, and wood. From any complete test record one can obtain important information concerning a material's elastics properties, the character and extent of its plastic deformation, and its yield and tensile strength and toughness [ROSATO, 1993]. The maximum tensile stress sustained by a specimen during a tension test is its tensile strength. When a material's maximum stress occurs at its yield point this stress is designated its tensile strength at yield [ROSATO, 1993]. The degree of crystallinity establishes the yield stress [MARK et.al., 1993].

1.2.2 Flexural strength

Flexural stress-strain testing determines the load necessary to generate a given level of strain on a specimen, typically using a three-point loading. The flexural strength, is also called the modulus of rupture [ROSATO, 1993].

Flexural testing is generally more convenient than tensile to assess the stiffness of rigid materials, but less convenient for strength measurement. In particular, across the thickness, the deformation changes gradually from a compressive mode to a tensile mode. If tensile and compressive behaviors of material are significantly different or if the specimen feature a variation of structure across the thickness, the quantities may not correlate well with corresponding tensile quantities [JEAN-MICHEL, 1991].

1.2.3 Impact strength

Impact strength is the property of a material to resist failure when subjected to a rapidly increasing applied force. It is expressed as the impact energy obtained from a particular impact test as the energy absorbed by the object during fracture at a very high testing rate.

The Izod impact test is the most widely used impact resistance test for plastics. The value of the impact strength usually increases with increasing temperature, especially in the region of the glass transition temperature (T_g). Orientation increases impact strength in the direction of orientation, but decreases it in the particular direction. [ROSATO, 1993; MARGOLIS, 1985].

1.3 Literature survey

This work was concerned with the reprocessing of Nylon 6,6, POM, PEI on the mechanical properties. The degradation of the materials can occur during the processing.

Nightingale (1976) showed that with 50% the re-used composition, the properties are reasonably constant after 6 passes of reprocessing; the amount of degradation would be classified as negligible and it would be difficult to detect any falling-off in mechanical properties.

Steppan et.al. (1991) studied the degradation of nylon 6,6 in the reactor and found that the slow moving material with longer residence times near the stationary reactor wall has not reached steady state and contributes to changing the small amounts of degraded product but does not affect the molecular weight. Arzak et.al. (1992) showed that the small variation of crystallinity of nylon6,6 and polyacetal does not produce a decrease in Young's modulus or any change in the other properties and the impact strength show a tendency to decrease as crystallinity increases.

Wyzgoski and Novak (1992) studied the morphology of nylon 6,6 and found the different appearances of the spherulites before and after reprocessing although no change in degree of crystallinity has been detected. The microscopy results indicate that the processing history causes a significantly decrease in the spherulites diameter.

Shah et.al. (1994) reported that nylon 6,6 shows a significant thermal degradation at 288 °C which only 35 °C above the melting point and it becomes more severe at a higher temperature. For polyacetal, it shows no decrease in melt viscosity up to 30 minutes at 191 °C and at high temperature polyacetal shows some decrease in melt viscosity indicating thermal instability at higher temperature. According to this work the recommended processing of nylon 6,6 and polyacetal are 271-280 °C, 191-204 °C, respectively.

Shriver et.al. (1994) reported that polymer degradation changes molecular structure, impacting rheological and mechanical properties. But did not significantly affect properties of polycarbonate which retained at least ten pass of reprocessing. Viscosity and swell ratio are the first indicators for degradation. The increase in melt flow rate is a measure of increased molecular degradation.

D.E. Floryan and I.W. Serfaty (1982) reported that the tensile strength and impact strength of Ultern1000 decreases as increase the temperature. At low shear rate, the resin exhibit Newtonian behavior and has high viscosity. The melt temperature of Ultern100 is about $357 \,^{\circ}$ C and the moisture should be reduced before the process.

Du Pont company reported (1996) that polyacetal are highly crystalline homoplastics. It is recommended for continuous use in air and water at temperatures up to 80 $^{\circ}$ C. The tensile strength of acetal homopolymer is 69 MPa and the izod impact strength is 75 J/m.

1.3 Objective

The objective of this research is to study the relationship between mechanical properties (tensile strength, flexural strength, and impact resistance) and number of passes.