CHAPTER 1

INTRODUCTION

1.1. General Introduction

The growth in the field of science and technology is being influenced by defence requirements and also due to development race in this particular field of an individual country amongst others. The growth in aerospace technology is also tremendously felt by both scientists and technologists especially in their search for the material which are advantageous in terms of its weight, performance and inertness to environment including therm-oxidative stability. The role of polymeric materials technologists were more demanding because of the inherent instability of organic polymers at elevated temperatures. Nevertheless the challenge provided a proper incentive for the growth of new and novel polymers which can outperform refractory metals and ceramics in specialized applications.

The advantages which can be achieved in respect to other classes of materials come from the following factors

(a) high strength/weight ratio
(b) comparable ease of processing

(c) wide structural variable materials
(d) flexibility of properties
(e) tailor-made structure

The premier requirement of thermally stable polymers is dictated by their high melting/softening temperature, resistance to oxidative/nonoxidative thermolytic processes and stability to other environmental parameters like radiation energy and chemical environment. The situation becomes more critical if we have to consider the case of processability which had been a impedance all-through in the search of an outstanding material with optimum stability, processability and economics. A typical example which explains the above contentions can be given for premier high performance plastics, polyimides, which exhibit an exceptional mechanical and thermal properties. Unfortunately, thermoplastic members of polyimide family are not readily processable and the finished parts are rather tend to be expensive requiring machining operations similar to metal fabrication.

However, before one can start looking into various aspects of development of these materials, one must carefully examine the meaning of the word thermal stability, its evaluation techniques and the fundamental structural and theoritical aspects governing them. A critical survey pertaining to the various aspects of the stability of high temperature polymers has been published recently[1].

1.1.1. Definition and Evaluation of Thermal Stability

From a practical stand point thermal stability is probably best defined as the temperature or temperature range that a material can withstand and still retain useful properties in a given application. In general, use temperatures are derived from property-time isotherms. By far the most widely used method for comparing thermal stabilities of experimental high-temperature polymers is dynamic thermogravimetric analysis (TGA). TGA data provide information about the thershold temperature at which major fragmentation occurs and is therefore an indication of the inherent stability of the polymer structure. Isothermal gravimetric analysis (IGA) is also used to some extent but is not as popular as TGA. Other methods of thermal analysis, such as differential thermal analysis (DTA), thermo-mechanical analysis (TMA), mass thermal analysis (MTA) and differential scanning calorimetry (DSC) have been widely applied to many high-temperature polymers.

In TGA, sample weight change versus temperature is recorded when the sample is heated in a thermobalance at a given temperature rise rate and in a specified environment (vacuum, air or inert atmosphere). This method has the advantage of being rapid and reproducible when the experimental conditions are carefully controlled. Since the temperature rise rates employed in this analysis are usually relatively rapid (2 - 30 °C/min), TGA curves are generally regarded as an index of short-term stability. Stabilities obtained from TGA curves are sensitive to experimental variables, such as particle size and temperature rise rate. Because of the sensitivity of TGA to experimental conditions, comparison of thermal stabilities can only be achieved by analysing samples of interest under identical conditions.

In the interpretation of dynamic TGA plots, the criteria that one uses is somewhat arbitary and it frequently happens that one criterion cannot be applied to all TGA curves. Most of the criteria refer to some recognizable features of the TGA plot. Examples of such criteria are (i) the 'knee' or temperature inflection point; (ii) the temperature of initial weight loss; (iii) the temperature where the rate of weight loss reached maximum; (iv) the temperature at which some present constant weight loss occurs; (v) the area under the weight loss curve; and (vi) the extrapolated onset temperature of decomposition, i.e., the intersection of tangent of same curve just prior to the major weight loss. Methods have been developed to calculate kinetic constants from TGA curves[2,3].

In isothermal gravimetric analysis (IGA), weight loss as a function of time is recorded at a specified temperature. One limitation of this method is that at high temperatures appreciable weight loss is incurred during the heat-up period before thermal equilibrium is reached. At lower temperatures, IGA is a valuable supplemental tool to TGA in that it can be used to obtain data on long term stability. It is not unusual to uncover stability differences by IGA that were not apparent by TGA. There is a rough correlation between dynamic TGA and IGA under certain conditions. This correlation relates to TGA residues at 500° and 550°C in air with IGA residues in air at 316° and 371°C, respectively[4].

An obvious limitation of both TGA and IGA is that they provide no information on such processes as softening or melting which do not involve weight changes. This limitation, however, is not too serious for most high temperature polymers which are infusible and undergo irreversible decomposition before they melt. Another limitation is that no information is provided on the reactions and processes that are responsible for the weight loss. For a basic understanding of thermal or thermoxidative stability, data on the volatile degradation products, their sequence and rate of formation as a function of temperature, and the changes that occur in structure and molecular weight of the residual material are required.

1.1.2. Theoritical Background

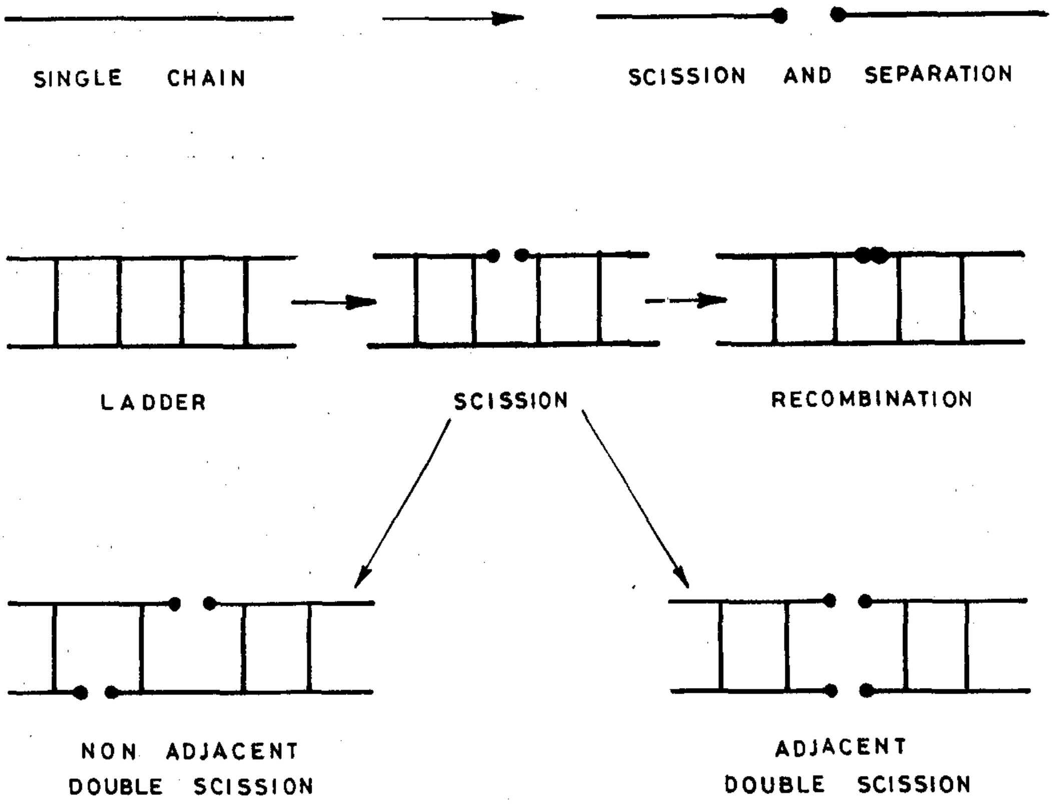
The greatest source of thermal stability is the primary bond energy that exists between the atoms in the chain. The strength of a chemical bond imposes an upper limit on the vibrational energy that a molecule may possess without bond rupture. Since heat increases the vibrational energy, the heat stability is related to the bond dissociation energy of the bond. Bond dissociation energy between two atoms can be determined by measuring the energy of dissociation into atoms or the heat of formation from the elements.

Polymers may also derive additional stability from secondary valence forces. The sum of these forces generally define what is called cohesion (i.e., attraction between neighbouring chains). These forces have a pronounced effect on the melting point and glass transition temperature. Secondary valence forces may arise as a result of several effects. Two of the more important of these are (i) dipole-dipole interaction (upto 8.7 KCals/mole) and (ii) hydrogen bonding (6 - 10 KCals/mole). The latter effect plays an important role in strongly polar polymers such as polyamides and polyurethanes.

High thermal stability in polymers can be achieved by making full use of resonance stabilization. Resonance stabilization of aromatic and heterocyclic structures, such as benzene or quinoxaline, contribute substantially to bond strength. The resonance energies of these cyclic structures range from 40 to 70 KCals/mole.

Another very important requirement for heat resistant polymers is high melting or softening temperatures. There are three general principles which,one may apply in order to arrive at high softening systems: (a) crystallization (b) crosslinking, and (c) chain stiffening. The first approach leads to thermoplastic materials which have more or less sharp and reversible melting points; the second approach produces three-dimensional unmeltable networks which are thermosetting and can withstand very high temperatures without softening. The third approach involves the synthesis and use of intrinsically rigid linear macromolecules which consist essentially of sequences of aromatic rings with only a few isolated single bonds.

Still another principle which has been proposed to enhance thermal stability in polymers is the ladder or double-strand concept[5,6]. The general idea is that a double-chain polymer, as opposed to single chain polymer, is not completely degraded by cleavage of a single chemical bond. This is illustrated graphically as follows (Scheme-1.1)



SCHEME - 1.1

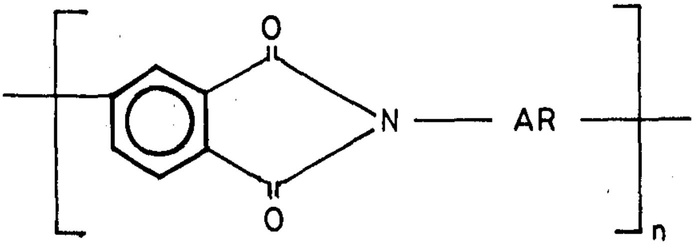
It is seen that when a break occurs at any point along a ladder polymer, the second strand keeps the entire polymer system intact and the close proximity of the fragmented part makes recombination probable. Furthermore, it is extremely unlikely that a second break would take place next to the first.

Degradation of polymers is often triggered at "weak links" in a polymer chain or network. Most high temperature polymers are prepared by condensation reactions and, consequently, may contain weak links in the form of end groups or structural moieties derived from possible by-product reactions. Consequently, lower degradation temperatures are observed than would be predicted on the basis of theoritical considerations outlined above. In such cases the kinetics of the reaction involving the weak link is likely to be the controlling factor.

1.2. Introduction to Polyimides

As mentioned earlier, the most versatile high temperature resistant organic polymer with wide commercial viability is POLYIMIDE. They are available in several forms suitable for different end product applications and uses. As far as back in '60s films and varnishes based on polyimides were commercialized, to be followed by suitable grade molding powders, laminating resins and metal-metal adhesives. Subsequently, fibers and foams have also been developed.

A representative structure of aromatic imide is illustrated below:



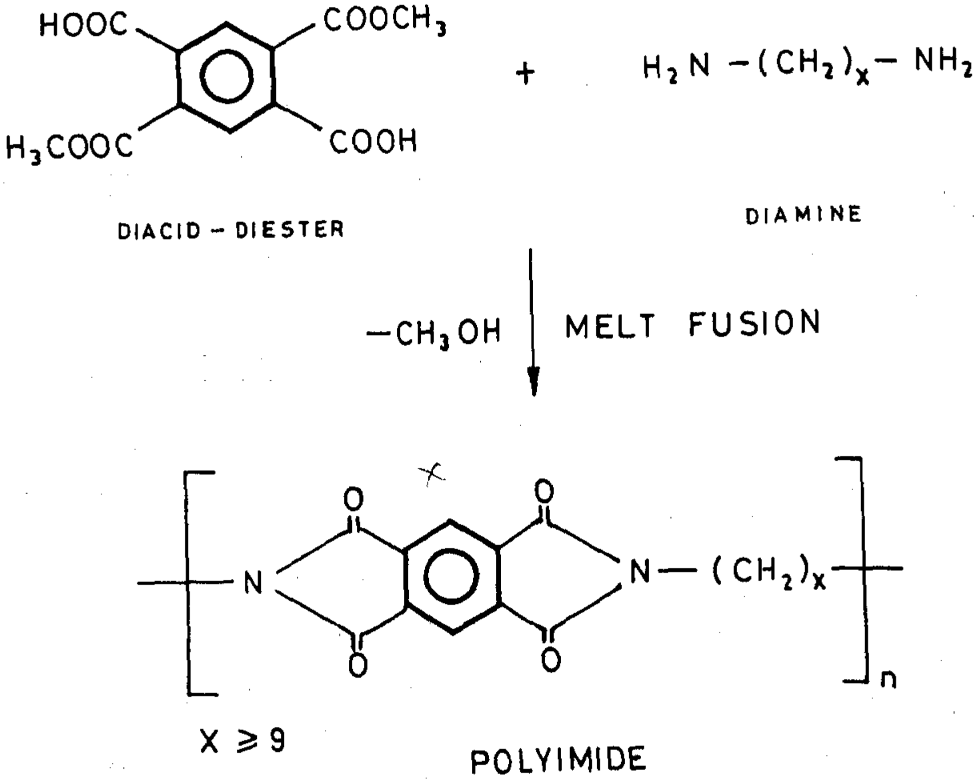
AR = Aromatic

and it is very stable both thermally and oxidatively. Polymers of this basic structure exhibit very high melting points, often above its decomposition temperature and the history of development of this family is the development of processable resin/polymer systems. Therefore, it will be highly appropriate if we look into the different types/classes of polyimides.

1.2.1. Condensation Polyimides

The first polyimides to be developed were prepared from aliphatic diamines by melt fusion of the salt formed from the diamine and tetra-acid or diamine and diacid/diester[7] (Scheme-1.2).

It was found that fusible pyromellitimides can only be obtained if the aliphatic diamines possess nine or more number of carbon atoms in a linear chain or seven in a



SCHEME-1.2

branched chain[8]. Due to the presence of these long chain aliphatic groups, the resultant polymers will be less thermo-xidative stable. The stability of these polymers can easily be enhanced by increasing the aromaticity. Wholly aromatic polyimides were soon developed[9-11]. It involves the synthesis of soluble polyamic acid precursor and a final cyclisation step to the required polyimide (Scheme-1.3). High purity reagents and solvents are essential for the synthesis of high molecular weight polymers along with the stoichiometric balance. Mixing details are also very critical. These polyimides are practically insoluble and infusible. The stability of polyamic acid intermediate is improved by using