

# Diamine Architecture Effects on Thermal Stability of Polyimides

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## ABSTRACT

Polyimides are the material of enormous scientific interest owing to their exceptional properties. This paper reports the synthesis, characterization and thermal properties evaluation of polyimides developed from structurally different diamines. The objective of the study was to develop the high temperature resistant materials by tailoring the properties of polyimides through structural modifications of diamine monomer. The research work involves the thermal measurements to evaluate and compare distinct conditions relevant to application of polyimides with high thermal stability. Most often polymer failed because of extended exposure at temperatures at which short-term exposure (few minutes) would not cause severe degradation. The dynamic TGA revealed the substantially high thermal stability of synthesized polyimides as their decomposition started above 400 °C with 5% weight loss temperature ( $T_5$ ) observed in the range of 496-540 °C. Isothermal TGA showed that the developed polyimides were capable to withstand elevated temperatures (400 °C) for relatively long period.

**Keywords:** Polyimides, Synthesis and Characterization, Thermal Stability, Tailoring of Properties.

## INTRODUCTION

Advances in the modern technologies are focused on reducing the cost of most demanding industrial processes by replacing metal, ceramic or glass with plastics. In this respect, variety of polymeric materials like poly-(olefins, ethers, ketones, sulphones, esters, amides, imides etc.) have been developed. However, polyimides have received special attention of scientists and engineers in the aerospace, automobile, microelectronics, optoelectronics and other advanced manufacturing industries as coatings, foams, matrices and gas separation membranes (Zhuo *et al.* 5141). The broad spectrum applications of polyimides is attributed to excellent combination of several beneficial properties: exceptionally high thermal stability and glass transition temperature, excellent mechanical strength and stiffness at elevated temperatures, low dielectric constant and refractive index, good chemical and radiation resistance (Akhter *et al.* 459) etc. These properties depend upon the chemical structure and intermolecular interactions of polyimide chains, hence can be improved further or attuned as required. This can be achieved mainly through structural modifications of monomers.

The ambition of the research presented here is to evaluate the properties of polyimides obtained from structurally different diamines. Main theme is to influence the charge transfer complex formation between alternating electron-acceptor (dianhydride) and electron-donor (diamine) moieties of polyimide chains, since it triggers their properties.

In our previous studies, polyimides were synthesized from phenyl and biphenyl containing diamines namely  $\alpha,\alpha'$ -bis(2-aminophenoxy)-p-xylene,  $\alpha,\alpha'$ -bis(3-aminophenoxy)-p-xylene and 4,4'-bis((4-aminophenoxy)methyl)-1,1'-biphenyl (Ashraf *et al.* 1001, Ashraf *et al.* 177, Ashraf *et al.* 46). It was observed that properties of resulting polyimides were influenced by structural variations. In continuation of our efforts

to investigate the monomer architecture effects on polyimide properties, a series of polyimides has been developed from structurally different diamine monomers for exploring/comparing their properties.

## OBJECTIVES

The paper describes the synthesis, structural characterization and properties evaluation of polyimides by dynamic and isothermal Thermogravimetric Analysis (TGA) along with Dynamic Mechanical Thermal Analysis (DMTA). The goals of the study were to monitor the effect of diamine structure variation on temperature resistance, thermal endurance, and glass transition temperature ( $T_g$ ) of polyimides. The selection of diamine monomers was based on the objective to check the effect of different side groups in the diamine structure on the thermal properties of resulting polyimides.

## METHODOLOGY

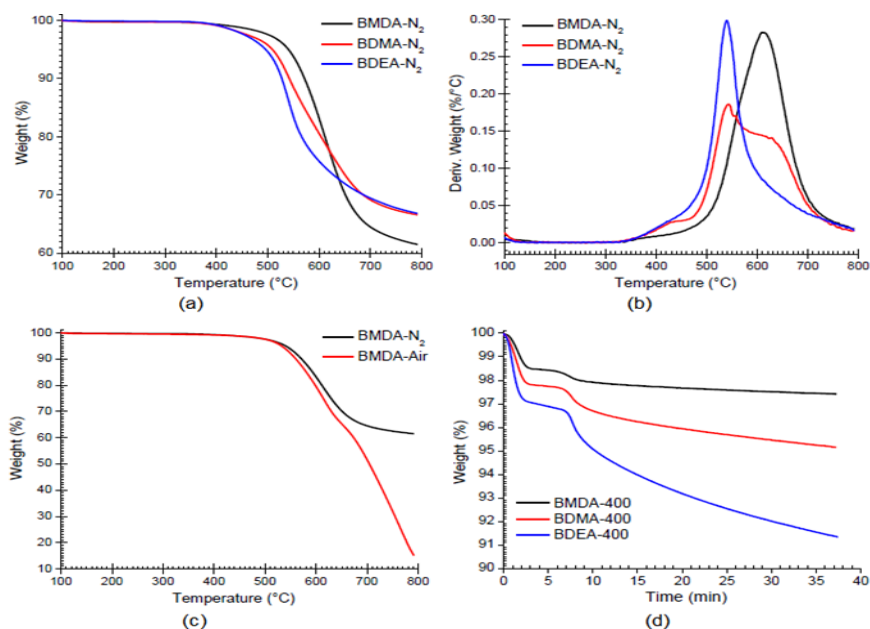
A series of polyimides was developed by reacting equimolar amounts of diamine with dianhydride following the condensation polymerization. The diamines and dianhydride selected for the study are: 4,4'-methylenedianiline (MDA), 4,4'-methylenebis(2,6-dimethylaniline) (DMA), 4,4'-methylene bis(2,6-diethylaniline) (DEA), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). The synthetic protocol is explained with the representative example of polyimide BMDA derived from BTDA and MDA. A 50 mL two-necked round bottom flask was charged with 0.198 g (1 mmole) of MDA and 4 mL of N,N-dimethylacetamide. The clear solution was obtained after complete dissolution of diamine. Then an equimolar amount of dianhydride (BTDA, 0.322 g, 1 mmol) was added to this solution in small portions with continuous stirring. The mixture was stirred for further 24 hrs at room temperature and a transparent, viscous polyamic acid solution was obtained. This polyamic acid solution was then casted on a clean aluminum weighing dish and cyclodehydrated to produce a fully imidized polyimide BMDA by curing with a programmed procedure: 70 °C (18 hrs for solvent removal in air circulating oven), 120 °C, 150 °C, 200 °C, 250 °C, 280 °C (1 hr. each in furnace). Finally, aluminum sheet was peeled off to get the polyimide film.

## RESULTS

The structural elucidation of the synthesized polyimides was carried out by Fourier transform infrared (FTIR) spectroscopic technique: both at polyamic acid stage and after imidization. The appearance of absorption bands around 1627  $\text{cm}^{-1}$  confirmed the formation of amide linkage in the pre-polymer. The conversion of pre-polymer to final polyimide was confirmed by the: i) shifting of carbonyl vibrations towards higher frequency i.e. from 1627 to 1720  $\text{cm}^{-1}$  in the characteristic symmetric stretching region of imide group, and ii) appearance of absorption bands at 1370  $\text{cm}^{-1}$  attributed to C-N-C moiety of imide ring (Table 1).

Three different types of TGA were performed to study the thermal behavior of synthesized polyimides: i) dynamic temperature scan under nitrogen, ii) dynamic temperature scan under air, and iii) isothermal under air. For this study, MDA was selected as reference diamine while DMA and DEA were used to check the effect of hydrogen atoms replacement with methyl and ethyl groups respectively, on the benzene rings of MDA. It was observed that substitution of benzene hydrogens with methyl groups led to decline in thermal stability and it decreased further with ethyl exchange as illustrated by comparative TGA and DTG plots of BMDA, BDMA and BDEA in Figure 1a and 1b respectively. The 5% weight loss temperature ( $T_5$ ) was decreased from 540 °C to 496 °C for BMDA and BDEA (Table 1). The shapes of TGA curves and DTG plots suggested one step thermal degradation mechanisms for MDA while two and three step pathways for DEA and DMA based polyimides respectively (Figure 1a, 1b). The dynamic TGA under the air atmosphere revealed the lower temperature resistance of polyimides in comparison with nitrogen as illustrated by TGA thermogram of Figure 1c. Isothermal TGA supported the findings of dynamic TGA. The isothermal TGA

graphic of Figure 1d is verifying the lower thermal stability/endurance of polyimides BDMA and BDEA as compared to relevant BMDA: inferred from their higher weight loss (%) after 35 minutes of experiment ( $W_{35}$ ).  $W_{35}$  at 400 °C was highest for BDEA (Table 1), which suggested its lowest thermal stability as revealed by dynamic TGA. The results of DMTA demonstrated that substitution of benzene hydrogens of MDA with methyl groups in case of DMA, triggered an increase in  $T_g$ . Interestingly, the replacement of methyl groups with ethyl units led to massive reduction in  $T_g$  rather than further increase, and even lower than reference MDA based polyimides (Table 1).



**Figure 1 (a-d).** Dynamic TGA (a, c), DTG (b) and isothermal TGA (d) thermograms of polyimides showing the variation in thermal stability with different side groups and atmosphere. (Dynamic: N<sub>2</sub>/Air, 20 °C/min; Isothermal: Air, ramp at 50 °C/min, at 400 °C).

**Table 1. FTIR, TGA and DMTA data of polyimides.**

Polyimide	C=O (cm <sup>-1</sup> )		C-N (cm <sup>-1</sup> )	T <sub>5</sub> (°C)	T <sub>10</sub> (°C)	R <sub>800</sub> (%)	W <sub>35</sub> (%)	T <sub>g</sub> (°C)
	Before imidization	After imidization						
<b>BMDA</b>	1625	1721, 1778	1368	540	572	62	2.56	293
<b>BDMA</b>	1628	1719, 1779	1370	509	542	67	4.76	315
<b>BDEA</b>	1629	1725, 1779	1370	496	527	67	8.46	284

T<sub>5</sub> = Temperature at 5% weight loss  
R<sub>800</sub> = Residual weight (%) at 800 °C

T<sub>10</sub> = Temperature at 10% weight loss  
W<sub>35</sub> = Weight loss (%) after 35 minutes of experiment

## CONCLUSION

The findings of the study to check the effect of side groups of diamines on thermal performance of polyimides are concluded to the fact that different substituents in the structure of diamine effectively played their part in governing the thermal properties of resulting polyimides. More specifically, the attachment of aliphatic side groups or chains made polyimide more prone to thermal degradation and ultimately lowered the thermal stability. The  $T_g$  of polyimides were improved by methyl substitutions on the benzene rings. The synthesized polyimides have the excellent potential to be used as high temperature resistant materials for applications under severe conditions where excellent thermal stability is desired for the extended period.

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