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Effect of polymer structure on glass transition temperature: A comparative DSC study of polyamide and polyester

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Abstract

Forest being the most important resource for the welfare of humankind, provide many tangible and intangible benefits to human beings. In many countries, people are dependent on forests for various products of which fuelwood is the main component. Fuelwood is the principal energy service provider to about 70% of the Indian population as it is extensively used for cooking and heating purposes. Lack of alternative sources of fuelwood makes the rural population mostly dependent on adjoining forest resources which ultimately results in the depletion of forest resources. The aim of present study was to examine the patterns of fuelwood consumption and their ecological implications in two villages namely village Chhani and village Lanchan of Bhaderwah forest division (J&K). The study was based on general survey and interview and it was observed that 12 plant species such as *Pinus wallichiana*, *Pinus roxburgii*, *Cedrus deodara*, *Quercus floribunda*, *Quercus leucotrichophora*, *Quercus semicarpifolia*, *Lyonia ovalifolia*, *Aesculus indica*, *Pyrus pashia*, *Indigofera species*, *Alnus nitida* and *Abies pindraw* were utilized as source of fuel wood in the study area. However, *C. deodara*, *Q. floribunda* and *P. wallichiana* were the most exploited fuel wood plant species. The preference for these species were due to ease of their availability and better fuel quality. Increase in fuel wood harvest caused intense forest degradation and biodiversity loss. The forests of the study area demand immediate attention in order to conserve the depleting forest structure. The policy makers must provide a sustainable solution to reduce the overexploitation of forest resources.

Keywords: Fuelwood consumption, forest degradation, biodiversity loss, rural dependency

1. Introduction

Thermal transition properties, particularly the glass transition temperature (T_g), play a crucial role in determining the performance and applicability of polymeric materials. The T_g reflects the temperature at which a polymer transitions from a rigid, glassy state to a more flexible, rubbery state, and is therefore a key parameter governing mechanical behavior, dimensional stability, and processing conditions [1-3].

Aromatic polymers such as polyamides and polyesters are widely studied due to their excellent thermal and mechanical properties. The thermal transition behavior of these polymers is strongly influenced by their molecular architecture, including backbone rigidity, intermolecular interactions, and the presence of functional groups. Aromatic polyamides exhibit high T_g values due to strong intermolecular hydrogen bonding between amide groups, which significantly restricts segmental chain motion. In contrast, aromatic polyesters contain ester linkages that impart greater flexibility to the polymer chain, resulting in lower T_g values and enhanced processability [4-6].

To further tailor the thermal properties of these polymers, structural modifications such as the incorporation of bulky aromatic units have been extensively explored. The introduction of naphthalene moieties into the polymer backbone increases chain rigidity and enhances thermal resistance by promoting conjugation and steric hindrance. Additionally, the presence of ether and amide linkages can influence chain mobility and intermolecular interactions, thereby affecting the glass transition behavior [7-8].

Although several studies have reported the thermal properties of modified polyamides and polyesters individually, direct comparative studies focusing on their thermal transition behavior are relatively limited. A systematic comparison between these two classes of polymers derived from similar monomer systems is essential to understand the influence of molecular structure on T_g [9-10].

In this context, the present study aims to investigate and compare the thermal transition behavior of aromatic polyamide and polyester derived from naphthalene-based monomers using differential scanning calorimetry (DSC). The study provides insights into how variations in polymer backbone structure and intermolecular interactions influence glass transition temperature and overall thermal performance.

2. Experimental

2.1 Materials and Polymer Preparation

The aromatic polyamide and polyester used in this study were synthesized from naphthalene-based monomers via solution polycondensation and interfacial polymerization techniques, respectively. All reagents were of analytical grade and used as received.

2.2 Synthesis of Polymers

The polyamide was prepared by reacting the diamine monomer N-(3,5-diaminophenyl)-4-(naphthalen-8-yloxy)benzamide with aromatic diacids in NMP using triphenyl phosphite and pyridine under nitrogen atmosphere at elevated temperature.

The polyester was synthesized by interfacial polycondensation of 3,5-dihydroxy-N-(4-(naphthalen-8-yloxy)phenyl)benzamide with IPC/TPC using a phase transfer catalyst in a biphasic system.

2.3 NMR Characterization

¹H NMR Spectroscopy

¹H NMR spectra were recorded at 400 MHz using appropriate deuterated solvents. Aromatic proton signals were observed in the range of 6.3-8.1 ppm, confirming the presence of phenyl and naphthalene units. The polyamide exhibited characteristic -NH- proton signals, while the polyester did not, confirming structural differences as shown in fig 1 and 2.

¹³C NMR Spectroscopy

¹³C NMR spectra were recorded at 100 MHz. The polyamide showed amide carbonyl signals at ~165-170 ppm, whereas the polyester exhibited ester carbonyl signals at ~170-175 ppm, confirming successful polymer formation as shown in fig 3 and 4.

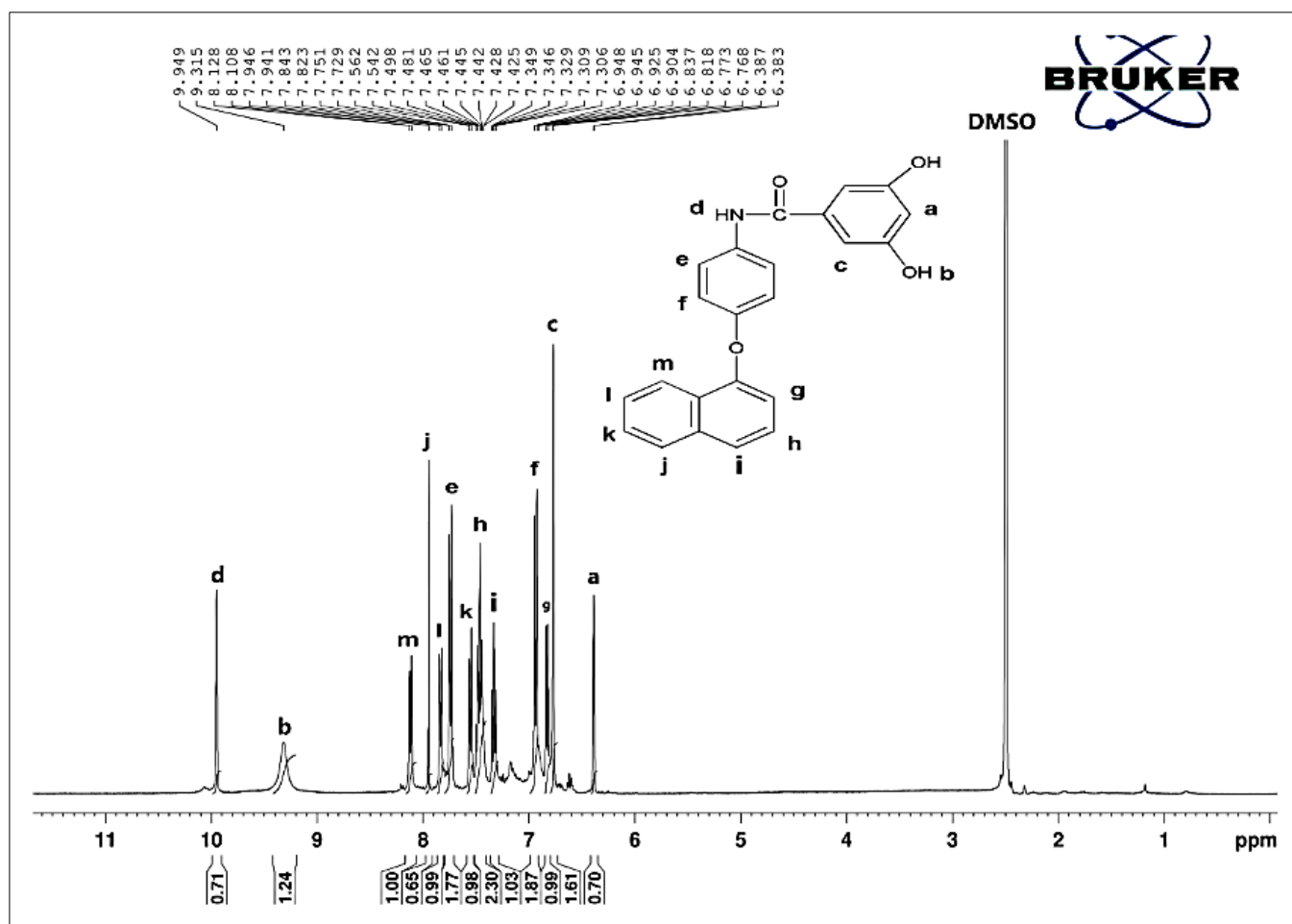


Fig 1: ¹H NMR spectrum of 3,5-dihydroxy-N-(4-(naphthalen-8-yloxy)phenyl)benzamide

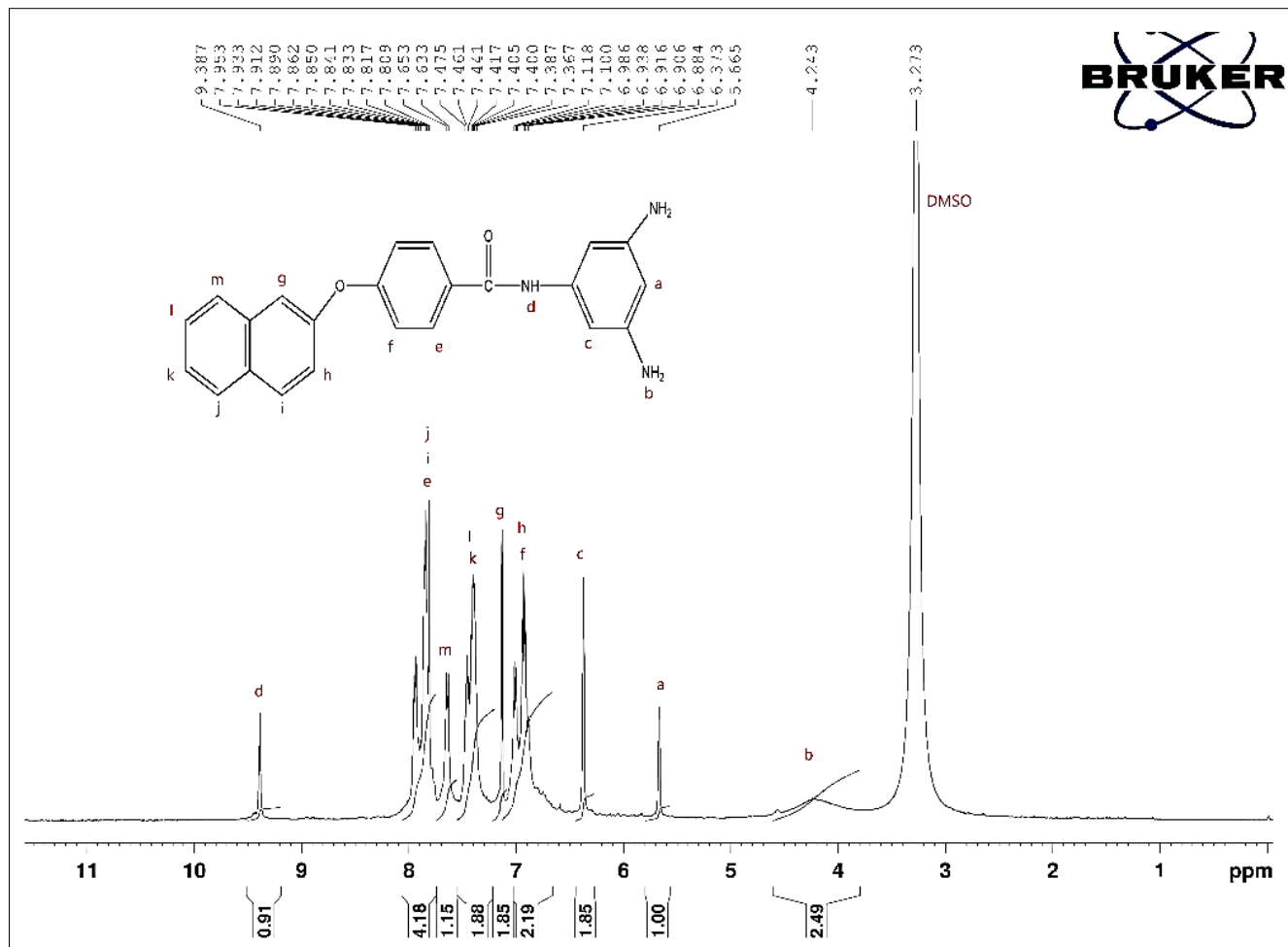


Fig 2: ¹H NMR spectrum of N-(3,5-diaminophenyl)-4-(naphthalen-7-yloxy)benzamide

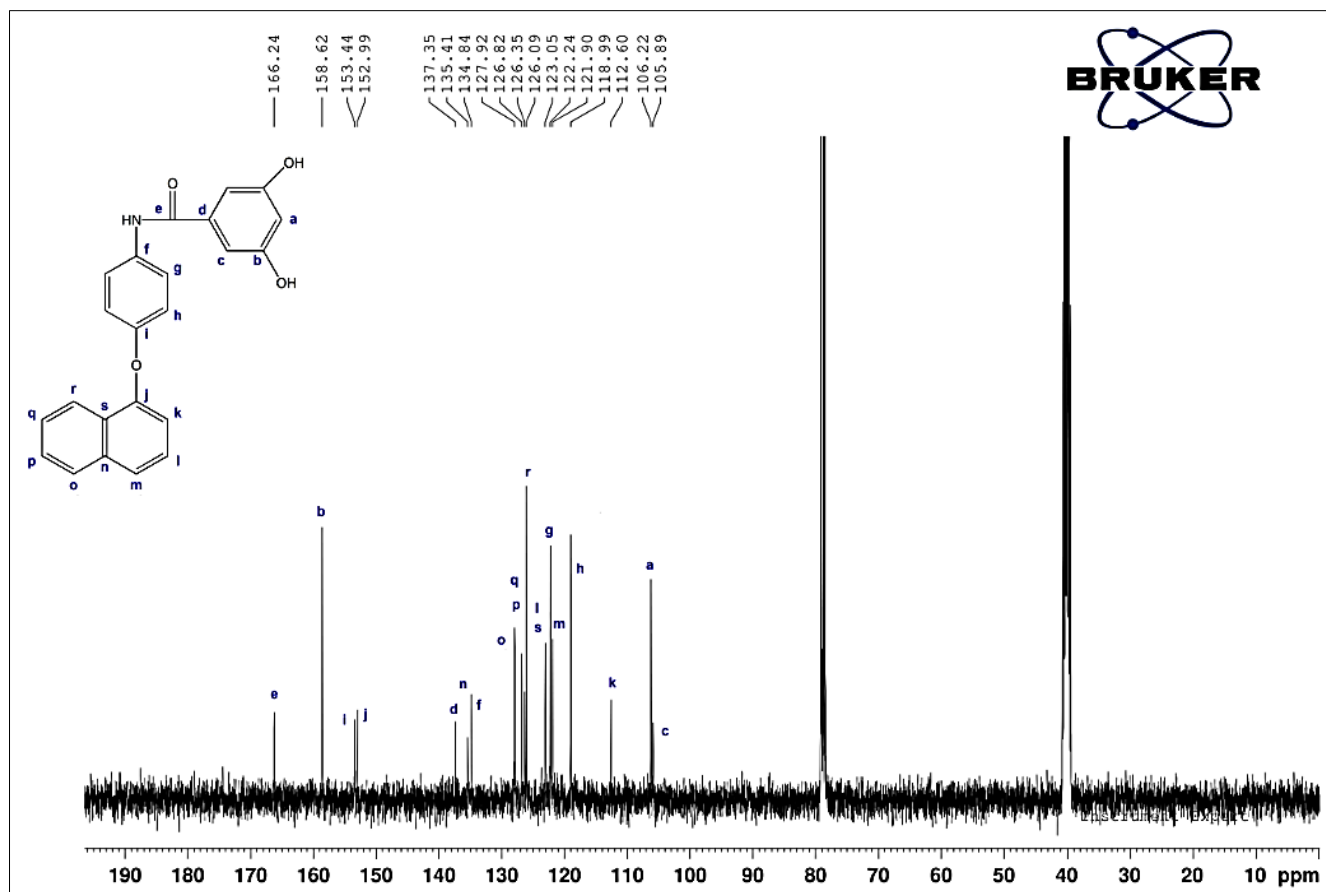


Fig 3: ¹³C NMR spectrum of 3,5-dihydroxy-N-(4-(naphthalen-8-yloxy)phenyl)benzamide

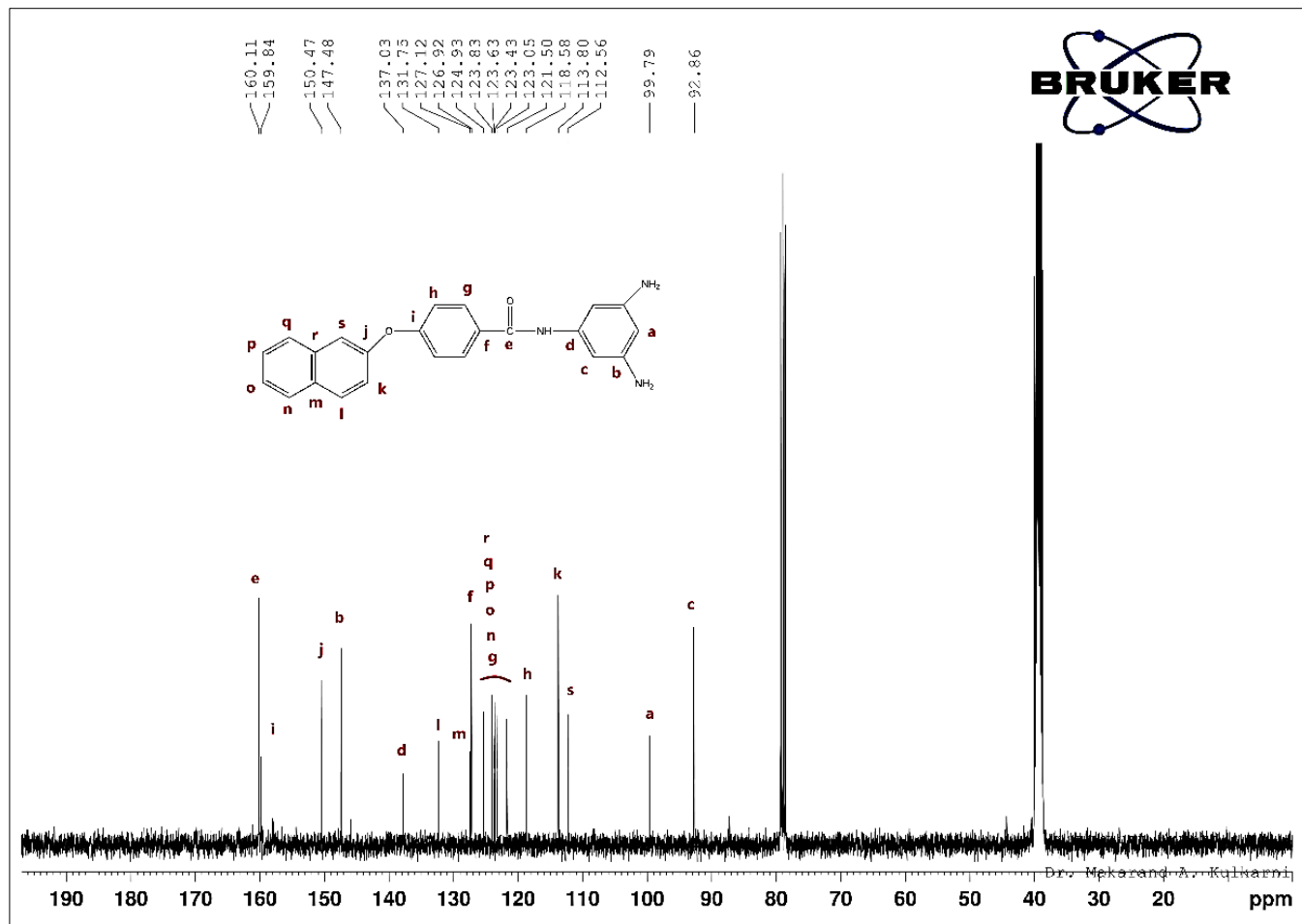


Fig 4: ¹³C NMR spectrum of N-(3,5-diaminophenyl)-4-(naphthalen-7-yloxy)benzamide

2.4 Differential Scanning Calorimetry (DSC)

DSC measurements were performed under nitrogen atmosphere at a heating rate of 10 °C/min. Samples were subjected to heating-cooling-heating cycles to eliminate

thermal history. The glass transition temperature (T_g) was determined from the midpoint of the heat capacity change in the second heating scan as shown in fig 5 and 6.

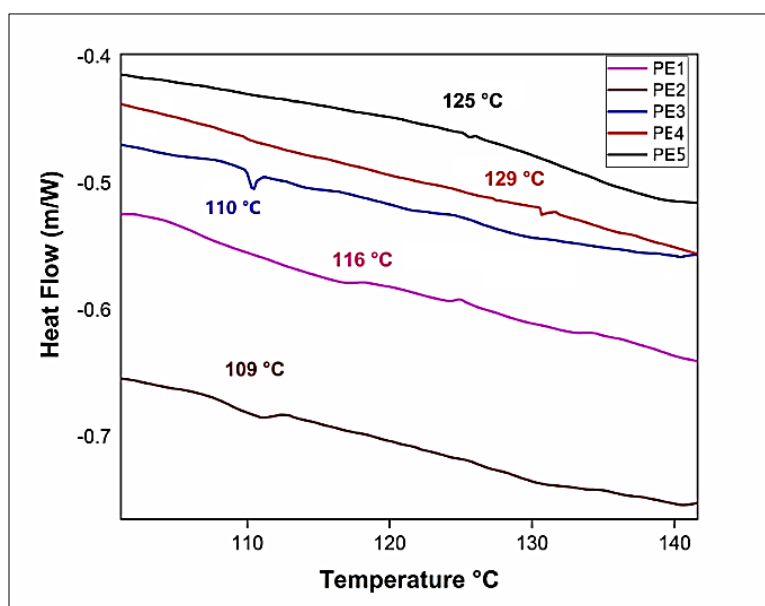


Fig 5: DSC curves of polyesters, PE-1 to PE-5

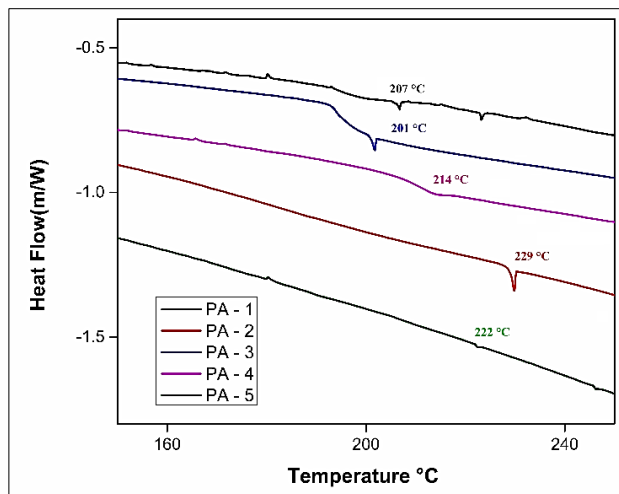


Fig 6: DSC curves of polyamides (PA-I to PA-V).

3. Results and Discussion

3.1 Thermal Transition Behavior (DSC Analysis)

The thermal transition behavior of the synthesized aromatic polyamide and polyester was investigated using differential scanning calorimetry (DSC). The DSC thermograms revealed a significant difference in the glass transition temperatures (T_g) of the two polymer systems, highlighting the strong influence of molecular structure on thermal properties. The polyamide exhibited remarkably high glass transition temperatures in the range of 265–300 °C, indicating a highly rigid polymer structure with restricted chain mobility. Such high T_g values suggest that the polyamide maintains its structural integrity even at elevated temperatures, making it suitable for high-temperature applications. In contrast, the polyester exhibited significantly lower T_g values in the range of 109–129 °C. The lower T_g indicates increased segmental mobility and reduced rigidity of the polymer chain. This difference in thermal transition behavior clearly reflects the variation in intermolecular interactions and backbone flexibility between the two systems.

3.2 Interpretation of T_g Difference

The significantly higher T_g of the polyamide is primarily attributed to the presence of strong intermolecular hydrogen bonding between amide groups. These hydrogen bonds act as physical crosslinks, restricting chain movement and requiring higher thermal energy to achieve the glass transition.

Additionally, the rigid aromatic backbone and the incorporation of bulky naphthalene moieties further limit chain flexibility, thereby contributing to the elevated T_g values observed for the polyamide system.

On the other hand, the polyester exhibits lower T_g due to the presence of flexible ester and ether linkages. These linkages reduce intermolecular interactions and increase chain mobility, allowing the polymer to undergo glass transition at lower temperatures. The absence of strong hydrogen bonding in the polyester further contributes to its lower T_g .

3.3 Structure-Thermal Transition Relationship

The comparative study clearly establishes that the thermal transition behavior of polymers is strongly governed by their molecular architecture. Polymers with rigid backbones and strong intermolecular interactions exhibit higher T_g values,

whereas those with flexible structures and weaker interactions show lower T_g .

Although the presence of naphthalene units enhances rigidity in both systems, the effect is significantly amplified in the polyamide due to the combined influence of hydrogen bonding and aromatic structure.

4. Conclusion

A comprehensive comparative study of the thermal transition behavior of aromatic polyamide and polyester derived from naphthalene-based monomers was performed using differential scanning calorimetry. The results reveal that the polyamide exhibits significantly higher glass transition temperatures (265–300 °C) compared to the polyester (109–129 °C), indicating a substantially higher degree of chain rigidity and restricted segmental motion.

The elevated T_g of the polyamide is attributed to strong intermolecular hydrogen bonding, rigid aromatic backbone, and the presence of bulky naphthalene moieties, which collectively enhance structural rigidity and reduce chain mobility. In contrast, the polyester exhibits lower T_g due to flexible ester and ether linkages, resulting in increased chain mobility and improved processability.

This study clearly demonstrates that the thermal transition behavior of polymers is strongly governed by molecular architecture and intermolecular interactions. The findings provide important insights for designing polymeric materials with tailored thermal properties, particularly for applications requiring a balance between thermal resistance and processability.

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