The Pyrolysis Behavior of Modified Poly-m-phenylene Terephthalamide by 4, 4’-diamino Diphenyl Sulfone

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Abstract: The modified Poly-m-phenylene terephthalamide (co-PMTA³) was prepared by polycondensation of m-Phenylenediamine, 4, 4’-diamino diphenyl sulfone and terephthaloyl dichloride with a mole ratio of 3:1:4 in N, N’-dimethylacetamide at low temperature. co-PMTA³ was soluble and expected to transform into fiber. The heat-resistance and thermal stability of co-PMTA³ were investigated by differential scanning calorimetry and thermogravimetric analysis, respectively. The results indicate that the co-PMTA³ possesses excellent heat-resistance and thermal stability with a glass transition temperature of 318.4 °C, initial thermal decomposition temperatures of 404.0 °C in air and 445.5 °C in nitrogen. In addition, the activation energy (Ea) of the decomposition process in air atmosphere was estimated by Ozawa-Flynn-Wall method which was be-tween 116.2 and 315.6 kJ/mol. The results indicate that the decomposition of co-PMTA³ air atmosphere is an overall reaction of multi elementary reactions.

1 Introduction

As one of wholly aromatic polyamides (aramids), the poly-m-phenylene terephthalamide (PMTA) possesses excellent thermal properties with a softening point temperature of 334 °C and a weight loss less than 10% under 400 °C [1, 2, 3]. However, the PMTA is insoluble in common organic solvents. The thermal properties and the solubility of wholly aromatic polyamides arise from their stiff rod-like macromolecule and amide linkages [4].

The modified poly-m-phenylene terephthalamide (co-PMTA³) was prepared via polycondensation of m-Phenylenediamine (mPDA), 4,4’-diamino diphenyl sulfone (4,4’-DDS) and terephthaloyl dichloride (TPC) with a mole ratio of 3:1:4 in N,N’-dimethylacetamide (DMAc) at low temperature. By incorporating 4,4’-DDS in backbone, the co-PMTA³ is soluble in DMAc and expected to transform into fiber by wet spinning. However, the thermal properties (heat-resistance and thermal stability) of co-PMTA³ are unclear.

According to the triangle theory of Heat resistance [5], the heat resistance of polymer has much to do with the crosslinking, crystallization and rigidity of their macromolecule. In addition, the thermal stability of the aromatic polymers depends on intermolecular forces and chemical-bond energy [6], which is measured by cohesive energy and activation energy respectively. Accordingly, the activation energy of degradation (Ea) is used to estimate the thermal stability and predict its durability, which reflects the resistance of decomposition in kinetics.

In this paper, the thermal properties of co-PMTA³ were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In addition, the Ea for decomposition process in air atmosphere was dealt with Ozawa-Flynn-Wall (OFW) method.
2 Experimental

2.1 Materials
The given ratio of monomers and intrinsic viscosity of co-PMTA3 sample is illustrated in Table 1. The sample was provided by Shanghai Tanlon Fiber Co., Ltd.

Table 1. Given ratio of monomers and intrinsic viscosities of sample

| Sample     | 4,4’-DDS: mPDA: TPC (mol) | Intrinsic viscosity (d/л) |
|------------|---------------------------|---------------------------|
| co-PMTA3   | 2.5: 7.5: 10              | 2.53                      |

* Intrinsic viscosity with dual capillary method in sulfuric acid at 25 °C.

2.2 Characterization
Glass transition temperature (Tg) of co-PMTA3 was characterized by DSC analyzer (STA449F3, Netzsch) from 50 to 400 °C at a heating rate of 20 °C/min, in N2 atmospheres.

The thermal degradation of co-PMTA3 was investigated by TG analyzer (STA449F3, Netzsch) from 50 to 900 °C at a heating rate of 5, 10, 15 and 20 °C/min, in air and N2 atmospheres.

3 Results and Discussion

3.1 DSC

Figure 1. DSC thermogram of the co-PMTA3 in N2

The DSC thermogram of co-PMTA3 is presented in Figure 1. The Tg can be used to evaluated the heat-resistance of polymer. The result indicates that the co-PMTA3 possesses excellent heat-resistance with a Tg of 318.4 °C, which is higher than that of PMIA [7, 9].

3.2 TGA
TG and differential thermogravimetric (DTG) curves in air and N\textsubscript{2} atmosphere are shown in Figure 2. By TG curves, there was no weight loss of co-PMTA\textsubscript{3} below 400 °C both in air and N\textsubscript{2} atmosphere, which indicated that no thermal decomposition occurred. By DTG curves, the decomposition process of co-PMTA\textsubscript{3} in air atmosphere was different with that of N\textsubscript{2} atmosphere.

The initial decomposition temperature (Td), the 5% weight loss temperature (T\textsubscript{5%}), 10% weight loss temperature (T\textsubscript{10%}) and residual weight at 650 °C and 900 °C in air and N\textsubscript{2} atmosphere are listed in Table 2.

| Atmosphere | Td (°C) | T\textsubscript{5%} (°C) | T\textsubscript{10%} (°C) | RW at 650 °C (%) | RW at 900 °C (%) |
|------------|---------|----------------|----------------|------------------|-----------------|
| N\textsubscript{2}  | 445.8   | 453.3          | 470               | 62.4             | 57.4            |
| Air        | 422.4   | 440            | 460               | 4.7              | 3.9             |

* RM is residual weight percentage

The co-PMTA\textsubscript{3} possesses excellent thermal properties with initial decomposition temperature of 442.4 and 445.8 in air and N\textsubscript{2}, respectively. It was almost no residual weight in air atmosphere but more than 50% residual weight in N\textsubscript{2} atmosphere at 900 °C. The results indicate that the thermal stability of co-PMTA\textsubscript{3} was better that that of PMIA[11].

3.3 Degradation Kinetic analysis
Polymer materials began to weight loss when the environment temperature increases to a certain degree, which means that the chemical combination of intermolecular and intramolecular began to break. The pyrolysis of solid polymer can be associated with the reactions which can be represented by the process as follows,

\[ A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}} \]  \hspace{1cm} (1)

According to the Arrhenius equation, there is a fundamental relation to express the thermal degradation in kinetics as follows,

\[
\frac{da}{dT} = A \exp(-Ea/RT)f(\alpha)/\beta
\]  \hspace{1cm} (2)

Where \( \alpha \) is the conversion values, \( da/dT \) is the rate of conversion, \( A \) is the pre-exponential factor, \( Ea \) is the activation energy of degradation (kJ/mol), \( T \) is the absolute temperature (K), \( R \) is the gas constant, \( f(\alpha) \) expresses a kinetic model function of the conversion of reactive group which depends on the particular decomposition mechanism, and the \( \beta \) is the constant heating rate.
It is complicated of solving the non isothermal decomposition kinetics equation (2) if solid-state process of decomposition in air involves multi-step elementary reaction superposition.

3.3.1 OFW method
The OFW method (T, 1965) can determine the activation energy (Ea) without a precise knowledge of reaction mechanism and the conversing function f (α). It is helpful to determine the activation energy by measuring of the temperature (T) corresponding to fixed the conversion values (α) from experiments with different heating rates (β), when the decomposition process involves multi-step elementary reaction superposition.

Integration of equation (2) from an initial temperature T₀, where the degree of conversion is α=α₀, to the peak temperature Tₚ, corresponding to α=αₚ, gives

\[ g(\alpha) = \int_{0}^{\alpha_p} d\alpha \int_{f_0}^{T_p} \exp(-Ea/RT) dT \]

\[ = \frac{AE}{R} \int_{f_0}^{T_p} \frac{d\alpha}{f(\alpha)} \] (3)

Where \( P(x) \) is temperature integration, and can be express as equation (4).

\[ P(\alpha) = \int_{-\infty}^{\alpha} \left( \frac{e^{-c}}{c^2} \right) dc \] (4)

Using the Doyle’s approximation, the function \( P(x) \) can be written as the following approximation:

\[ \lg P(\alpha) = -2.315 - 0.4567 \frac{Ea}{RT} \] (5)

Taking logarithms equation (3) and substituting equation (5) to it, gives

\[ \lg = \lg \left( \frac{AE}{Rg} \right) - 2.315 - (0.4567 \frac{Ea}{RT}) \] (6)

Plotting log (β) against 1/T, according to equation (6) for a fixed degree of decomposition α, the activation energy (Ea) can be obtained.

3.3.2 Ea by OFW method

![Figure 3. TG in air with heating rate 5, 10, 15 and 20 K/min](image)
The thermal degradation curves carried out at heating rates 5, 10, 15 and 20 °C/min are shown in Figures 3.

In this paper, the conversion values are 0.045, 0.098, 0.142, 0.200, 0.305, 0.446, 0.602, 0.790, and 0.891. The fitting straight lines are showed in Figure 4.

![Figure 4. OFW plots of co-PMTA3 at different conversion values (α)](image)

The linear correlation function fit well with point at different conversion values. That indicates that the OFW method is applicable to our system. The activation energy (Ea) of thermal degradation for co-PMTA3 could be obtained by the OFW method from the slope (0.4567Ea/RT) of linear fitting of log (β)- 1000/T at a fixed conversion values. The corresponding activation energies calculated from the slopes are displayed in Figure 5.

![Figure 5. Activation energies (Ea) obtained by OFW](image)

According to the results of the activation energy depicted in Figure 5, we can see that the calculated activation energies change with conversions and temperatures. The result indicates that the process of decomposition in air involves multi-step elementary reaction superposition. It seems that the pyrolysis of co-PMTA3 is easy at the beginning with the minimum activation energy of 116.2 kJ/mol. It becomes more difficult with the maximum activation energy of 315.6 kJ/mol when the conversion (α) was 0.2. This might be that the some of structural units in backbone are stable in oxygen and require higher activation energy for their further degradation.
4 Conclusions

By incorporating 4,4’-DDS in backbone, the co-PMTA₃ is soluble in DMAc and expected to transform into fiber by wet spinning. Meanwhile, the co-PMTA₃ possesses excellent heat-resistance and thermal stability with a glass transition temperature of 318.4 °C, initial thermal decomposition temperatures of 404.0 °C in air and 445.5 °C in N₂.

In addition, the active energy (Eₐ) of the decomposition process in air atmosphere was estimated by OFW method which was between 116.2 and 315.6kJ/mol and changed with the conversions and temperatures. The decomposition of co-PMTA₃ air atmosphere is an overall reaction of multi elementary reactions.

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