



Composition optimization of PEEK/PEI blend using model-free kinetics analysis

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ARTICLE INFO

Article history:

Received 23 June 2010

Received in revised form 10 August 2010

Accepted 12 August 2010

Available online 19 August 2010

Keywords:

Poly(ether ether ketone)

Poly(ether imide)

Miscible blend

Thermal stability

Model-free kinetics

Activation energy

ABSTRACT

We report here the investigations on the thermal and thermo-oxidative degradation kinetics of a miscible high performance polymer blend poly(ether ether ketone)/poly(ether imide) (PEEK/PEI) with various compositions, measured in argon and air medium, respectively. The derivative thermogravimetric results indicate two-stage decomposition for both thermal and thermo-oxidative degradation for the entire composition of PEEK/PEI blend. Interestingly, the PEI addition is found to enhance the thermo-oxidation rate of PEEK. The effective activation energy (E_{α}) as a function of conversion (α) is found for both the processes using model-free kinetics. The model-free kinetics results reveal that the blend with 50% PEI content show high E_{α} value and the differential scanning calorimetry results corroboratively show a significant change in crystallinity for this PEI composition. Based on these results, the blend with composition 50/50 (PEEK/PEI) is suggested to have optimum thermal stability.

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1. Introduction

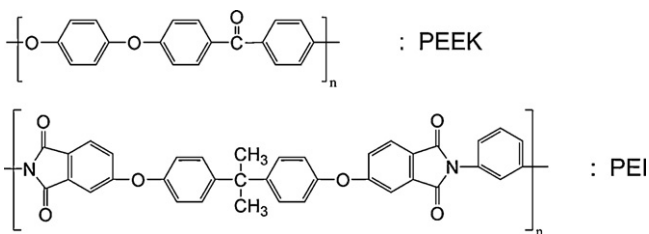
Poly(ether ether ketone) (PEEK) is a high performance engineering semicrystalline thermoplastic having excellent chemical resistance and superior mechanical properties [1–5]. It is suitable for use as a matrix material in the preparation of thermoplastic composites owing to its good adhesion to glass and carbon fibres [6,7]. However, because of its relatively low glass transition temperature (T_g) of around 145 °C, the modulus of these materials decreases at elevated temperatures [5]. On the other hand, poly(ether imide) (PEI) is an amorphous polymer with comparatively high T_g of around 215 °C [5,6]. But, PEI has a lower chemical resistance than that of PEEK and cannot be used above its T_g [5,7]. Blending of these two polymers combines the complimentary properties of both of them and hence PEEK/PEI blends have been the subject of several investigations for more than two decades [2,4–17]. Now, it is a proven fact that PEEK and PEI are molecularly miscible in the amorphous state [2,4–7].

With the improved T_g , the PEEK/PEI blend is a suitable matrix resin in the preparation of high performance composites for aerospace applications as well as for conventional spare parts in aircraft components [17–19]. For this, good thermal and oxidation stability and retention of physical properties at high temperatures

are required because they can be subjected to drastic thermal conditions in service or during repair [3,20,21]. Thus, degradation studies on PEEK/PEI blend in various environments and the associated kinetics are of paramount importance. The common method for determining the behavior such materials at high temperatures is by studying their thermal degradation at elevated temperatures using thermogravimetric analysis (TGA) [22]. Despite of many aspects that have been studied on PEEK/PEI blends [2,4–17], the thermal decomposition studies on PEEK and PEI using TGA are mostly directed in understanding its degradation temperature, and thereby to correlate with other physical and mechanical properties [17,23].

Temperature changes can stimulate a variety of chemical and physical processes in polymeric systems like thermal degradation, cross-linking, crystallization, glass transition, etc. [24]. Thus, the nature of the polymer degradation kinetics is complex as they include information about simultaneously occurring multiple steps. Results of the ICTAC kinetics project [25] suggested that isoconversional methods could provide a solution to this challenge. In the recent years, the model-free kinetics method, which is based on Vyazovkin's theory for the kinetics studies of complex reaction [26–28] has become a popular method in obtaining a reliable and consistent kinetic information on the thermal degradation process in many polymers and polymer composites [24,28–34]. In the model-free kinetics, the dependence of effective activation energy (E_{α}) on the degree of conversion (α) is found through which single-step or multi-step nature of the decomposition mechanism can be confirmed [33–35]. The model-free kinetics also enables

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Scheme 1. Chemical formulas of PEEK and PEI.

the prediction of reaction kinetics over a wide temperature range [28,29,33,34].

Furthermore, the variation of E_{α} as a function of α is considered as one of the important parameters to understand the thermal stability of the polymers [35,36]. A polymer with higher E_{α} value is expected to be more stable [35,36]. The E_{α} value of the blend can be higher or lower than that of both the individual polymers from which it was obtained [37–39] or to one of them [34,40,41]. Incorporation of nanomaterials to polymers has shown to increase the E_{α} value of the resulting polymer nano-composites [28,35,36].

Nevertheless, to the best of our knowledge, there are no scientific works to date that employs model-free kinetics analysis to understand the thermal stability of PEEK/PEI blends. Scientific curiosity has thus stimulated us to investigate whether PEEK/PEI blend could be optimized based on model-free kinetics. In the present study, using the model-free kinetics [26–28], we provide the effective activation energy (E_{α}), the conversion rates and the degradation time as a function of temperature for the thermal and thermo-oxidative degradation for various compositions of PEEK/PEI blend and thereby suggest the optimum blend composition. The differential scanning calorimetry (DSC) results corroborate the model-free kinetics data.

2. Experimental

2.1. Sample preparation

Granular PEEK-grade Victrex 450G was purchased from Victrex, U.K. and the PEI-grade Ultem 1000 was obtained from General Electric Plastics, Europe. Both PEEK and PEI were used as received and were dried for 48 h at 120 °C under vacuum. Blending was performed on a corotating twin-screw extruder at ca. 370 °C. The strand leaving the extruder was quenched in a water bath, air dried and chopped in to granulates. Blends with weight ratios of PEEK/PEI 100/0, 90/10, 80/20, 70/30, 50/50, 30/70 and 0/100 were prepared. These blends are designated, respectively as P₀, P₁₀, P₂₀, P₃₀, P₅₀, P₇₀ and P₁₀₀ (where the subscripts represent the wt% of PEI). The blends were subsequently injection molded at ca. 380 °C in to square plates (60 mm × 60 mm × 3 mm). The chemical structure of the PEEK and PEI is shown in Scheme 1.

2.2. Characterization

Although the main aim of the work is to understand the thermal decomposition kinetics of PEEK/PEI using model-free kinetics as applied to its TGA results, we have first performed differential scanning calorimetry (DSC) measurements to identify the glass transition temperature (T_g) of the various proportions of this blend and thereby to make sure that the blend used in the present investigation is miscible. The T_g has been taken as the inflexion temperature of the heat flow, the peak temperature of the endothermic heat flow as melting temperature (T_m) and the peak temperature of the exothermic heat flow (during cooling) as the crystallization temperature (T_c). For DSC experiment, DSC Q200 (TA instruments)

was employed. The instrument was calibrated using indium standard. Samples of ~6 mg were weighed and sealed in aluminum sample pans and were heated above their melting temperature for 5 min and then cooled to erase the thermal history. Then the samples were reheated with a heating rate of 20 °C/min and the T_g and T_m were taken from the second heating traces and T_c from the corresponding cooling traces.

Thermogravimetric analysis was performed using a TGA (Mettler-Toledo TGA/SDTA 851^e) instrument in the temperature range 30 to 1100 °C. The instrument was calibrated using a Mettler-Toledo total calibration procedure with respect to the indium and aluminum standards. Samples (~6 mg) for TGA measurements were placed in 70 μ L alumina crucibles. The buoyancy effect in TGA has been accounted for by performing empty pan runs and subtracting the resulting data from the subsequent sample mass loss data. Thermal decomposition experiments were carried out in dynamic conditions using the nominal heating rates of 5, 10, 15 and 20 °C/min both in argon and dry air atmosphere (flow rate in each case was maintained at 50 mL/min). In the temperature program, an initial 10 min isothermal segment allowed the furnace to purge with argon/dry air and then the temperature was ramped to 1100 °C at the specified heating rate. The T_{onset} is the onset temperature corresponding to the start of degradation (the intersection of the extrapolated base lines with tangents drawn in the inflection points of the TG curve), T_{max} is the temperature at the maximum rate of degradation and R_{900} is the percentage residue at 900 °C. Mettler-Toledo STAR^e software (ver 9.0) was used to perform the model-free kinetics calculations that provide activation energy as a function of extent of conversion. This software also helps for life-time predictions of the measured sample.

2.3. Model-free kinetics (MFK)

The rate of a thermal reaction depends on the extent of conversion (α), temperature (T) and time (t). Here, the degree of conversion (α) is defined as the ratio $(m_i - m)/(m_i - m_f)$ where m_i , m and m_f refer to the initial, actual and final mass of the sample. For each process, the reaction rate as a function of conversion, $f(\alpha)$ is different and must be determined from the experimental data. The dependence of α on temperature is customarily expressed as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where $k(T)$ is the rate constant and $f(\alpha)$ is the reaction model [27]. Depending on the reaction mechanism, the reaction model may take various forms. The temperature dependence of the rate constant is expressed in terms of Arrhenius equation as

$$k(T) = A \exp\left(\frac{-E}{RT}\right) \quad (2)$$

where T is the temperature, R is the gas constant, A is the pre-exponential factor and E is the activation energy.

Substitution of Eq. (2) to Eq. (1) yields

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (3)$$

As mentioned earlier, the degradation of polymers tends to demonstrate complex kinetics that cannot be described by Eq. (3) alone throughout the whole temperature region [28,35]. The model-free kinetics method is based on the realization that the activation energy indeed depends on the extent of conversion (α) but they are always same at a particular conversion independent of the heating rate used. Thus, model-free kinetics (MFK) method is also called as an isoconversional method [28]. The isoconversional methods may be best known through their most popular representatives, the methods of Friedman [42], Ozawa [43] and Flynn and

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