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Thermal decomposition properties of polymer fibers

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Abstract

Polymer fibers are one of the main substances used for the reinforcement of plastic composites. Their characteristics are very important, especially the thermal properties of the reinforcement materials and matrix polymers. In this work, the thermal properties of polymer fibers were investigated using DSC/DTA/TG. The thermal decomposition kinetic parameters of polypropylene fibers were then evaluated by non-isothermal DSC/DTA/TG techniques. The data from the thermal analysis for the polymer fibers would be a reference fingerprint for thermal analysis.

Keywords: Thermal decomposition; Polymer fibers; Thermal analysis

1. Introduction

Textile fibers are the building blocks of yarns and fabrics. Traditionally the term fiber referred to a continuous structure whose length was several hundred times its diameter and which possessed a balance of functional and harmonious properties sufficient to make it suitable for processing and end-use service. Today the term fiber is no longer limited by the concept of continuity. The physical form of today's textile fibers fall into three broad categories: staple, tow, and continuous filament. The significant usage of fibers in all three of these forms are attributable, in a large measure, to the effects of polymer fiber producers. The use of the staple, tow, or continuous filament fiber forms as raw materials to produce a garn or a yarn modification is a vital link between fiber and fabric. Generally, staple and tow are processed by the textile-mill-products industry and filament by the man-made-fiber manufacturer. The present study aimed at the thermal decomposition properties of polymer fibers, such as polypropylene, Nylon 6, and Kevlar 29, which were investigated by DSC/TG. The kinetic parameters for the decomposition of polypropylene were also evaluated by both the DSC/TG non-isothermal techniques.

2. Experimental

Samples of polymer fiber were purchased from manufacturers. The physical properties of the polymer fibers are listed in Table 1. DSC/TG curves of polymer fiber were obtained using a TAI 200 thermal analyzer (DSC, model 910) to study the thermal decomposition of polymer fibers. Approximately 3 mg of each sample was heated at 5–20 °C min^{-1} heating rate under a static air atmosphere. Thermogravimetric analysis (TG, model 951) was also used in this work.

3. Results and discussion

DSC curves of Nylon yarn, Kevlar, and polyester can be seen in Figs. 1 and 2. In the Nylon yarn curves,

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Table 1
Physical properties of polymer fibers

Polymer fibers	Density (g/cm^3)	Heat resistance (°C)	Glass transition temperature (°C)	Melting point (°C)	Crystallized temperature (°C)
Nylon 6	1.14	150	40–87	220	173
Kevlar 29	1.44	240	90	–	–
Polypropylene	0.91	100	−17	168	–
Polyester	1.40		69–80	265	

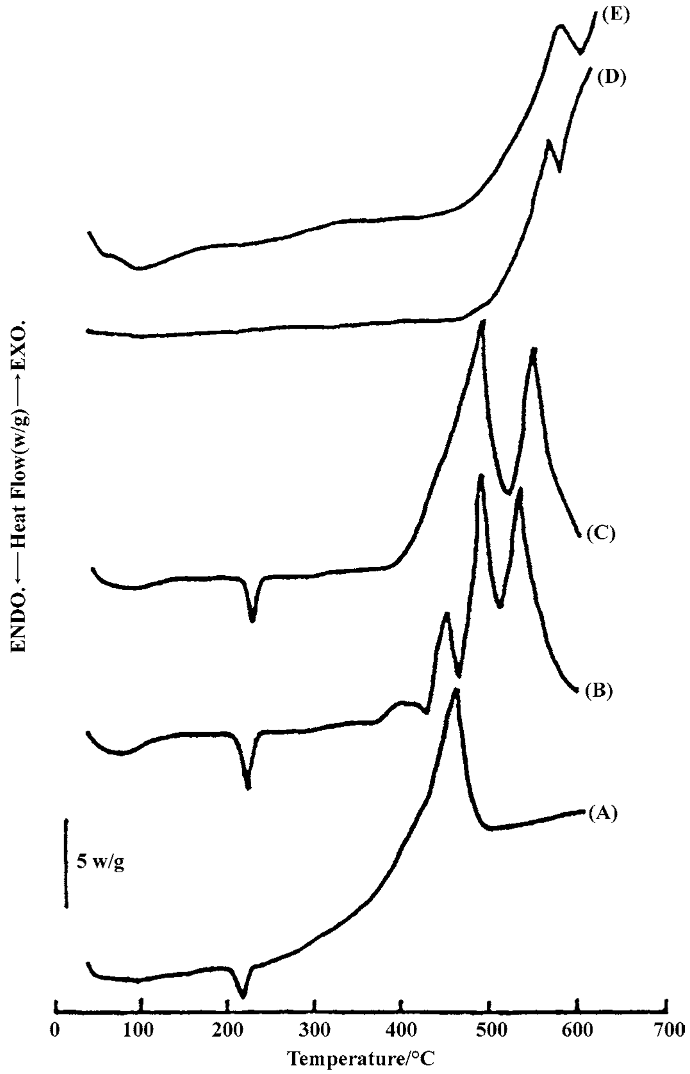

Fig. 1. DSC curves of Nylon and Kevlar fiber at a 10 °C min^{-1} heating rate under static air atmosphere. (A) Nylon/carbon commingled yarn, (B) Nylon filament yarn, (C) Nylon textured yarn, (D) Kevlar filament yarn, (E) Kevlar staple fiber.

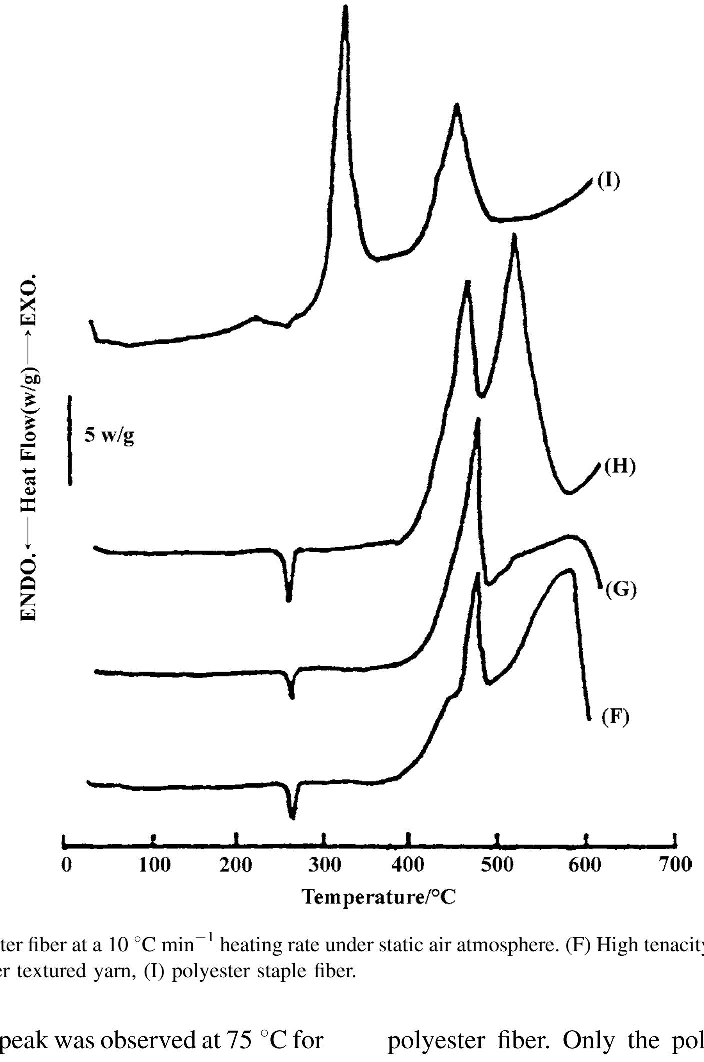

Fig. 2. DSC curves of polyester fiber at a 10 °C min^{-1} heating rate under static air atmosphere. (F) High tenacity polyester, (G) stainless steel/polyester 20/80, (H) polyester textured yarn, (I) polyester staple fiber.

one broad endothermic peak was observed at 75 °C for Nylon filament yarn and Nylon/carbon commingled yarn, which corresponds to the glass transition temperature (T_g). The T_g of Nylon textured yarn was close to 93 °C. DSC curves of Nylon yarn also indicated a sharp endothermic peak with the minimum at 223.7, 221.9, and 212.5 °C, respectively, after which decomposition occurred. In the Kevlar curves, only the Kevlar staple fiber showed a broad endothermic peak at 90.6 °C corresponding to the glass transition temperature. Then from 100 to 450 °C, the DSC curves indicated an endothermic peak at a 10 °C min^{-1} heating rate under a static air atmosphere. The starting decomposition occurred at 450 °C. The DSC curves of polyester fibers showed an endothermic peak at 259.4 and 265 °C, respectively, before the melting point of polyester fiber. Only the polyester staple fiber possessed a glass transition temperature around 85 °C, with the decomposition of the polyester staple fiber taking place immediately after melting.

The DSC/TG curves of polypropylene filament yarn under a static air atmosphere and at a heating rate of 5–20 °C min^{-1} are shown in Fig. 3. The DSC curve of polypropylene filament yarn indicated an exothermic peak at 173 °C corresponding to the melting point of polypropylene filament yarn. The polypropylene filament yarn then starts decomposing after 200 °C.

The kinetic parameters have been derived based on the peak temperature–program rate relationship, or the so-called non-isothermal techniques [1–3]. Ozawa [4], Flynn and Wall [5], and Doyle [6] have shown that the activation energy of a thermal decomposition process

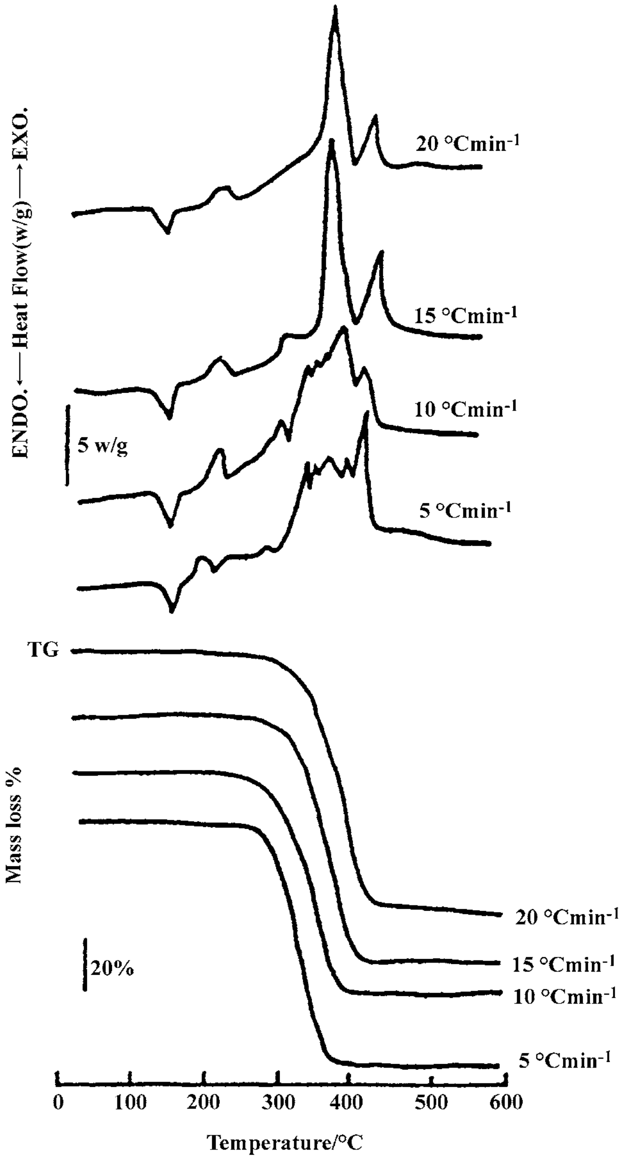

Fig. 3. DSC/TG curves of polypropylene fiber at 5–20 °C min^{-1} heating rate under static air atmosphere.

can be determined directly from a series of TG curves obtained at different heating rates. The method developed by Flynn is a quick and simple method for determining the activation energies directly from the mass loss vs. temperature data at several heating rates. It is not to be expected that any single kinetic expression would be applicable to a wide range of decomposition processes. A kinetic analysis method based on the assumption that the decomposition obeys first-order kinetics was later generalized. The Arrhenius activation energy is determined from a plot of the logarithm of heating rate vs. the reciprocal of the absolute temperature at a constant conversion level. The slope of these plots with an average value of 0.457 is used in Eq. (1):

$$\frac{\mathrm{d}\log(h)}{\mathrm{d}(1/T)} = -\left(\frac{0.457}{R}\right)E \qquad (1)$$

Table 2
Kinetic parameters of polypropylene fiber[a]

Mass loss percentage (%)	$-\gamma_a$	Activation energy (kJ mol^{-1}), $B = 0.457$	E/RT	b (re-evaluated)	Activation energy (re-evaluated) (kJ mol^{-1})	Average activation energy
1	0.991	76.4	17.05	0.490	71.3	78.4 ± 7 (calculated under 20% mass loss)
3	0.997	85.5	18.53	0.484	80.7	
5	0.994	86.4	18.43	0.484	81.6	
10	0.990	88.5	18.48	0.484	83.6	
15	0.988	85.3	17.57	0.487	80.0	
20	0.981	79.5	16.24	0.497	73.1	
25	0.995	83.2	16.82	0.492	77.3	
30	0.993	85.1	17.06	0.490	79.4	
40	0.999	94.1	17.00	0.491	79.9	
50	0.983	94.1	18.43	0.484	88.9	
60	0.995	111.5	21.67	0.474	107.5	
70	0.996	104.3	20.07	0.477	100	
80	0.991	97.2	18.45	0.484	91.8	
90	0.987	106.1	19.91	0.478	101.4	

[a] γ: Correction coefficient for linear regression analysis of Kissinger plot; $b = \log P(E/RTi) - \log P(E/RTi - 1)$.

The value of 0.457 was obtained using a series of iterations. The value of *E*/*RT* was calculated, where *E* is the approximate activation energy and *T* is the temperature obtained using a program rate near the middle of the range at a constant mass loss (nominally 10 °C min^{-1}).

Table 2 contains the activation energies of decomposition for polypropylene filament yarn that were evaluated by non-isothermal techniques. The activation energies for decomposition of the polypropylene filament yarn ranged from 71 to 84 kJ mol^{-1} as determined by the dynamic TG methods.

A kinetic analysis method based on the assumption that the decomposition mechanism obeys first-order reactions was devised. That the calculated activation energy is independent of the reaction mechanism does not hold for the later stages and should be used with caution. An upper limit of 10% decomposition is suggested. Although 20% mass loss is justified in certain cases, it is strongly advised that calculations be made at several different levels of decomposition, for example 5, 10, 15 and 20% [7]. In this study, the activation energy of decomposition under an upper limit of 20% ranged from 71 to 84 kJ mol^{-1}, with a standard deviation of 2.43.

4. Conclusion

Almost all the measurements that can be done at different temperatures can be expanded into thermal analysis, and any series of thermal analysis techniques can be combined for valuable multiple-parameter measurements. In order to realize the processing temperature and time of the fiber–resin composite systems, the investigation on thermal properties of resin and fibers is worth noticing. The thermal properties data for Nylon, Kevlar, polyester fiber, and polypropylene fiber would be a fingerprint reference for the processing of fiber–resin composites. The activation energy of decomposition under an upper limit of 20% for polypropylene fiber ranged from 71 to 81 kJ mol^{-1}, with a standard deviation of 2.43 which is acceptable in thermal analysis.

Acknowledgement

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