The Influence of Light on the Thermal Decomposition of Polypropylene Fibers

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ABSTRACT: The influence of exposure to artificial light (ultraviolet and visible spectrum) on the thermal degradation process of polypropylene fiber has been investigated. The activation energy E as a kinetic parameter of the fiber thermal decomposition has been defined by means of the Flynn–Wall and Freeman–Carroll methods. The fiber melting temperature range was also defined. The investigations have been made on the basis the of thermal gravimetric analysis and differential thermal gravimetric analysis curves determined at various heating speeds, in the temperature range from 100°–600°C. It was found that thermal stability of polypropylene fiber is reduced by light treatment (i.e., fiber softens and melts at a lower temperature). Activation energy values determined for thermal decomposition of the fiber samples exposed to the influence of light are considerably higher than the values determined on unexposed samples. The decomposition process of aged fiber is more complex and occurs in a larger temperature range. Both the methods used show almost similar results. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2237–2244, 1999

Key words: polypropylene fiber; UV light treatment; thermal stability; thermal decomposition kinetics

INTRODUCTION

Although polypropylene (PP) macromolecules do not contain chromophore chemical groups able to absorb light, PP fibers are very sensitive to photodegradation; this is one of the main disadvantages in using these fibers. Ultraviolet (UV) part of the white daylight spectrum is a significant factor of fiber decomposition. Photon energy of the shortest wavelength in sunlight spectrum ($\sim$ 290–300 nm) is $\sim$ 290 kJ mol^{-1} photons, which is higher than the strength of the most molecular links in PP fiber. Even the traces of residual catalysts in a polymer (in concentrations of 10^{-3} to 10^{-4} mol L^{-1}), as well as a weak CT *complex* created between the polymer and molecular oxygen, significantly raise the photosensibility.[2] This explains that even extremely pure PP fibers are also prone to photodegradation.

It can be assumed that the fiber aging caused by light have repercussions on the thermal properties of fiber. Generally speaking, the thermal stability of PP fibers, in relation to polyamide and polyester fibers, is still relatively low. It is manifested in a relatively low glass transition temperature T_g ($-10°$ to $-15°$C), low softening temperature (149° to 151°C), and low melting point T_m (165° to 170°C). According to Madorsky,[3] PP thermal decomposition in vacuum occurs in the temperature range of 336° to 366°C, and for the activation energy E in vacuum the same author quotes the value of 245 kJ mol^{-1}. In the present article, the authors studied the effect of UV light on the thermal stability of the PP fibers and on

Table I Sample Designation According to Time of Light Treatment

Sample Mark	0	1	2	3	4
Time of light treatment (h)	0	200	500	803	1005

the kinetics of thermal decomposition. To have a deeper understanding of this matter, systematic investigations are conducted and reported in the present article.

EXPERIMENTAL

The investigations have been made with a standard type of PP fiber, of a high isotacticity index ($\sim$ 98%), and 14.5 dtex fineness. Because the fiber is a commercial one, it contains a UV stabilizer (0.1% Irganox + 0.1% polystyrene). The fiber samples were exposed to the influence of light in the wavelength region of 290–800 nm (UV and visible spectrum) for various periods of time (Table I). Xenotest apparatus, with a xenon bulb emitting the light of the intensity of 180 kLx and a power of 1000 W m^{-2}, was used. The tempera-

ture in the illumination chamber was 25°C ± 2°C, and relative humidity of the air was 65% ± 2%. According to the apparatus producer's specifications,[3] illumination cycle of 24 h under the given condition's equals 10 days of exposure to sunlight under average weather conditions and moderate climate zone. Thermal decomposition of the samples was investigated in the temperature range from 100° to 600°C, in argon flow (flow of 3 mL s^{-1}), using a DuPont TGA 951 apparatus. Sample mass varied from 4.5 to 7.5 mg. The thermal gravimetric analysis (TGA) recording of decomposition was conducted nonisothermally at the following heating speeds: 5 K min^{-1}, 10 K min^{-1}, 15 K min^{-1}, and 20 K min^{-1}. Furthermore, the variation of mass in time (i.e., the differential curve dm/dt) was recorded [differential TGA (DTGA)].

RESULTS AND DISCUSSION

The results obtained are presented in graph form and in the tables. Figure 1 shows the TGA curves of thermal decomposition of sample 1 (exposed to light for 200 h), obtained at various heating speeds. Figure 2 shows DTGA curves of the same PP fiber sample, obtained at the same heating speeds. The figures show that the exposed PP

Figure 1 TGA curves of PP fibers exposed to light for 200 h.

Figure 2   DTGA curves of PP fibers exposed to light for 200 h.

sample has been thermally decomposed in a one-step process. Thermal decomposition of the same, but unexposed PP fiber, was investigated in an earlier article.[4] Results show that the shape of TGA and DTGA curves of the exposed PP samples and the unexposed ones (see ref. 4) is approximately the same, but slightly shift to lower temperatures.

Activation energy E of thermal decomposition of PP fiber samples is determined using Flynn–Wall and Freeman–Carroll methods, to get an insight into thermal decomposition kinetics.

Isoconversion analysis according to Flynn-Wall[5] and Baker[6] asks for the investigation of thermal decomposition with various sample heating speeds β. The equation that defines E is as follows:

Figure 3   Plots of log β versus $1/T$ of sample 1 (200 h of illumination) at different conversion levels X.

Figure 4 Plots of log β versus $1/T$ of sample 2 (500 h of illumination) at different conversion levels X.

Figure 5 Plots of log β versus $1/T$ of sample 3 (806 h of illumination) at different conversion levels X.

Figure 6 Plots of log β *versus* $1/T$ of sample 4 (1005 h of illumination) at different conversion levels X.

$$E = -\frac{R}{b}\left(\frac{d(\log \beta)}{d(1/T)}\right) \quad (1)$$

where E is activation energy (J mol^{-1}), R is gas constant (8134 J mol^{-1} K^{-1}), T is temperature at a certain constant conversion level (K), β is heating speed (K min^{-1}), and b is constant [$\cong 0.457 \pm 0.004$ for $29 < (E/RT) > 46$]. On the similar

way Zhou and Wu studied the thermal decomposition kinetics of poly(phenylene sulfide amide).[7]

The numerical values of derivative expression in eq. (1) [$d(\log \beta)/d(1/T)$] are obtained on the basis of direction coefficients of the straight lines shown in Figures 3–6. The most probable straight lines for certain (chosen) conversion levels are determined using the least-squares method. Par-

Table II Activation Energy E (kJ mol^{-1}) of the Thermal Decomposition of PP Fibers at Various Conversions (X)

X (%)	Sample 0[4] (Untreated)	Sample 1 (200 h of illumination)	Sample 3 (500 h of illumination)	Sample 4 (806 h of illumination)	Sample 5 (1005 h of illumination)
5	83.57	112.14	118.72	168.56	189.56
10	90.73	125.54	118.42	169.55	176.74
15	97.79	129.71	123.67	166.58	190.95
20	96.64	140.49	130.18	172.47	177.53
30	101.17	149.92	141.78	170.20	166.86
50	110.81	155.38	152.86	160.89	186.49
70	129.32	152.22	149.23	161.08	191.86
90	128.43	146.83	149.46	161.77	201.00

Figure 7 TGA curves of PP samples. (1) Untreated sample; and (2–5) samples exposed to light for 200, 500, 806, and 1005 h.

ticular single straight line corresponds to a definite conversion level $X(X_i = $ const.) and shows the dependence of log β upon the $1/T$ (reciprocal temperature), at which the chosen decomposition level occurs.

The figures show that the lines calculated for various levels of thermal decomposition (X_i in Table II) are not parallel. Depending on the level of conversion, parallel and unparallel sections occur. This change in straight line slope proves that the thermal decomposition of the samples tested is a complex process and even a heterogeneous one. Decomposition kinetics of PP samples exposed to UV light for various periods of time is not the same. E is determined from the direction coefficient, and results are presented in Table II.

For the sake of comparison, in the table are also presented the E values determined for the untreated PP fiber (sample 0).[4]

Data in Table II show that E values of the samples exposed to the influence of UV light are considerably higher than the values determined on untreated PP sample. At a given conversion X, the activation energy of thermal decomposition rises up with the prolongation of the time in which the sample is exposed to light. This occurred particularly in the initial phase of decomposition. Similar to that of the untreated fiber, E of samples 1 and 2 also rises with the rise of the decomposition level X, but tended to be constant when conversion was $> 50\%$. The same has not occurred on samples 3 and 4, which are treated

Table III   Temperatures Typical for the PP Fiber Thermal Stability Characterization

Sample Mark	0	1	2	3	4
Time of light treatment (h)	Untreated	200	500	806	1005
Begin of softening (°C)	152	148	143	140	138
Peak of melting (°C)	166	165	165	164	163
End of melting (°C)	168	168	168	167	168
Temperature range of melting (°C)	16	20	25	27	30
Temperature at conversion ($X = 5\%$) (°C)	425	417	415	403	395
Temperature at conversion ($X = 90\%$) (°C)	470	470	468	470	469
Temperature range of decomposition (°C)	45	53	53	67	74

Figure 8 Graphic presentation of the Freeman–Carroll method of determination of activation energy. (0) Untreated sample; and (1–4) samples exposed to light for 200, 500, 806, and 1005 h.

with light for a longer period of time. These fibers are considerably damaged, and their thermal decomposition is more complex.

During the nonisothermal decomposition of PP fibers, various conversion products are created. E rises with the number of conversion products (i.e., types of molecular groups). A significant rise in the activation energy for thermal decomposition of the samples exposed to light, as opposed to E of the untreated sample, indicates that thermal stability of the fiber is reduced by light treatment and becomes more complex. Even at low conversion levels of samples 3 and 4, more conversion products are created than in the case of total decomposition PP fiber, which was not exposed to light.

Thermal decomposition of PP fiber is considerable influenced by UV light. This is confirmed in Figure 7, which shows TGA curves of fiber samples exposed to the influence of light during various periods of time. Obvious disparateness of the curves indicates the differences in the kinetics of thermal decomposition of individual samples.

The points in which individual TGA curves leave the basic line show the initial temperature of PP sample in thermal decomposition. Table III presents temperatures typical for PP fiber thermal stability characterization. Data obtained show that thermal stability of PP fiber is reduced by the influence of light. Thermal softening and thermal decomposition begin at a lower temperature.

Activation energy of thermal decomposition is also determined using the Freeman–Carroll method to check data obtained using the Flynn–Wall method and to compare the methods. This relatively simple method is based on the Freeman–Carroll[8,9] and Anderson–Freeman[10] equations:

$$\frac{-\dfrac{E}{2.3R}\Delta(T^{-1})}{\log W_r} = -n + \frac{\Delta\,\log(dW/dt)}{\Delta\,\log W_r} \quad (2)$$

where E is activation energy (J mol^{-1}), T is temperature (K), n is order of reaction (presumed: reaction of the first order), $W_r = W_c - W$ (W_c is mass loss at total reaction and W is mass loss at temperature T), and dW/dt is rate of mass loss.

This method uses a DTGA curve determined at a set heating speed. Activation energy is calculated from the slope (direction coefficient) of the

Table IV   Comparison of the Values of Activation Energy Determined by the Freeman-Carroll and Flynn–Wall Methods

Sample	Time of Exposure to Light (h)	E (kJ mol^{-1}) (Freeman–Carroll method) (conversion X = 10–50%)	E (kJ mol^{-1}) (Flynn–Wall method) (conversion X = 10–50%)
0	0	98.65	99.48
1	200	135.92	140.03
2	500	129.50	133.36
3	806	152.54	166.34
4	1005	193.02	179.71

straight line resulting from eq. (2), shown in Figure 8. DTGA curves are recorded at the heating speed of 10 K min^{-1}. Line direction coefficient can be represented as $(-E/2.3R)$. Activation energies obtained in this way are given in Table IV, together with the values calculated using the Flynn–Wall method. Table IV shows that, for the thermal decomposition range X = 10% to X = 50%, both of the methods give approximately the same activation energy values. The Freeman–Carroll method also showed that the lowest activation energies are recorded for thermal decomposition of the samples unexposed to the influence of light, whereas the highest value is obtained for the sample that was illuminated for the longest period of time (1005 h). That means that both of methods show the same influence of light treatment on thermal decomposition of the fiber.

CONCLUSIONS

- PP fibers exposed to the influence of light (UV and visible spectrum) have been thermally decomposed in a one-step process. Decomposition is a complex process and, at certain conversion levels, it uses the same mechanism.
- Thermal stability of PP fibers is reduced with the influence of light (i.e., their thermal softening and decomposition begin at a lower temperature).
- Activation energies determined for thermal decomposition of the fibers exposed to the influence of light are considerably higher than the values determined on the untreated fiber. With the longer period of illumination time, activation energy rises. That is the result of the numerous decomposition products, meaning that the decomposition process becomes more and more complex.

Both the methods used give the same kinds of influence of light on PP fiber thermal decomposition kinetics.

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