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Improvement of TG Resolution by Heating Rate Conversion Simulation Method

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Introduction

Thermogravimetry (TG) is widely used for the quantitative analysis of polymer materials thermal resistance test and of the polymer blend components. However, each mass change may not be measured accurately due to the reactions occur at similar temperatures while separated determination is performed for blended materials by TG. In this case, TG resolution improvement method using low heating rate measurement or CRTA (Controlled-Rate Thermal Analysis) is applied; however, there is an issue of decreased measurement efficiency due to the longer measurement time.

As a solution of this problem, Heating Rate Conversion Simulation Method is proposed. This method calculates the activation energy ΔE of each reaction with regard to the decomposition reactions from TG measurement results, performs time-temperature conversion using calculated ΔE, and converts to low heating rate measurement data. TG resolution can be improved by this method (Figure 1).

In this study, the analysis result of the cotton-polyester blended yarn blending ratio is reported as an analytical example using the Heating Rate Conversion Simulation Method. Evaluation of the ratio of cotton and polyester components was not possible from TG raw data. However after the conversion this TG raw data to the slower heating rate measurement data by the Heating Rate Conversion Simulation Method, accurate blending ratio for cotton and polyester is obtained.

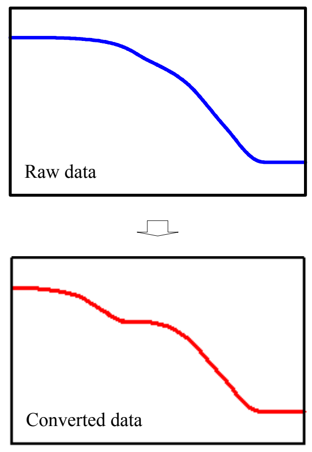

Fig.1 TG curves for raw data and converted data

Heating Rate Conversion Simulation Method

Figure 2 shows an overview of conversion when multiple reactions follow Arrhenius principles. Since each slope in the Arrhenius plot of multiple reactions corresponds to ΔE, the signal values of the heating rates can be shifted to signal values of different heating rates. In general, phenomenon at high temperatures tend have a large ΔE. If high heating rate data is converted to low heating rate data, the temperature resolution improves. This is one target of this simulation method. On the other hand, since the conversion can shift also to high heating rates, simulations can be performed at high, or conversely, very low heating rates, where actual measurements would be difficult.

Figure 3 shows the algorithm for heating rate conversion simulation. It detects the DTG signal peaks and detects overlapping. If there is no overlapping, activation energy (ΔE) is calculated as is. When there is overlapping, peaks are separated and then ΔE is calculated for each peak. Using these ΔE values, the Arrhenius reaction is estimated. Time - temperature conversion is performed and the differences in heating rate are converted using a temperature shift. The TG signal is integrated and output.

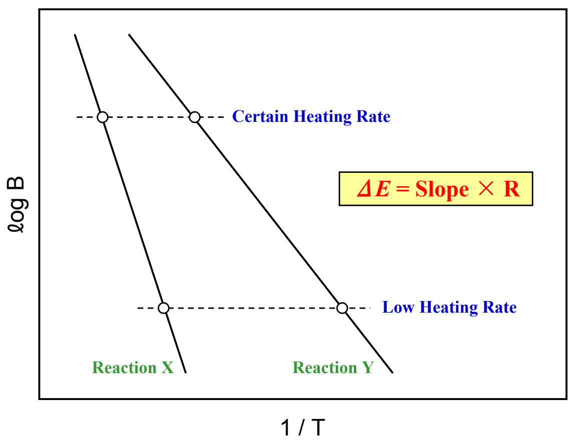

Fig.2 Arrhenius Plot for Multiple Reactions
B: heating rate
T: temperature
R: gas constant
ΔE: activation energy

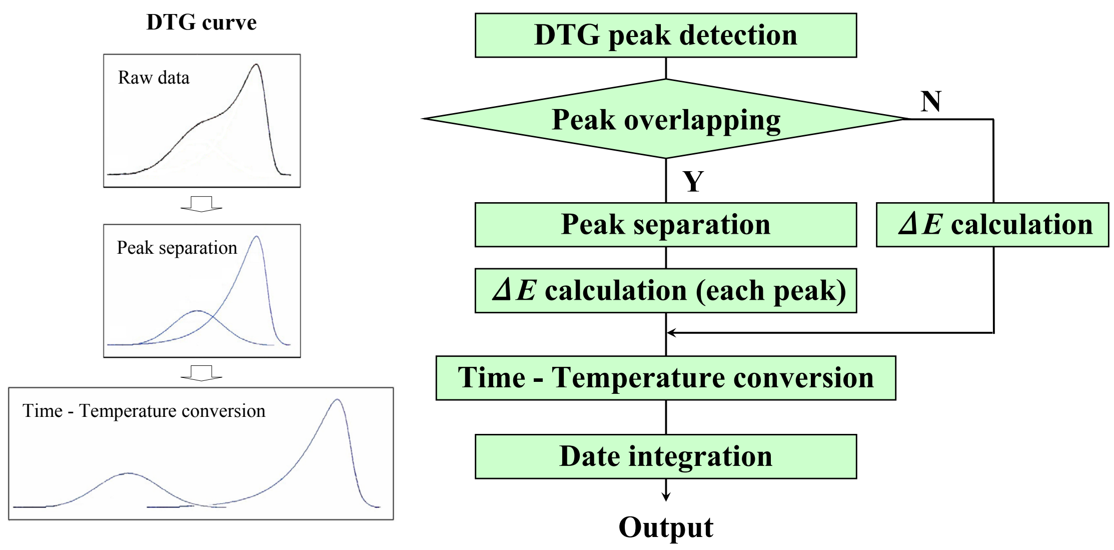

Fig.3 Algorithm for Heating Rate Conversion Simulation Method

Measurement Results

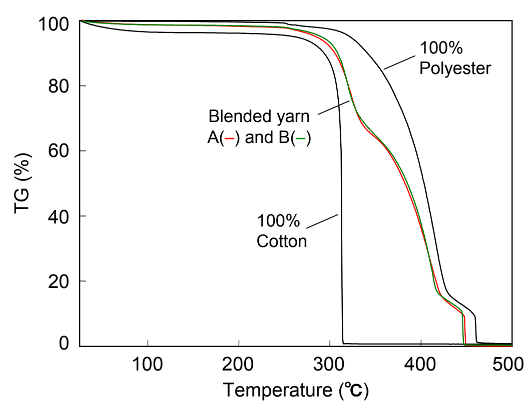

Fig.4 TG curves for the blended yarn A and B, 100% cotton, and 100% polyester
Heating rate : 10 ℃/min
: Blended yarn A, polyester : cotton = 67.3 : 32.7
: Blended yarn B, polyester : cotton = 65.1 : 34.9

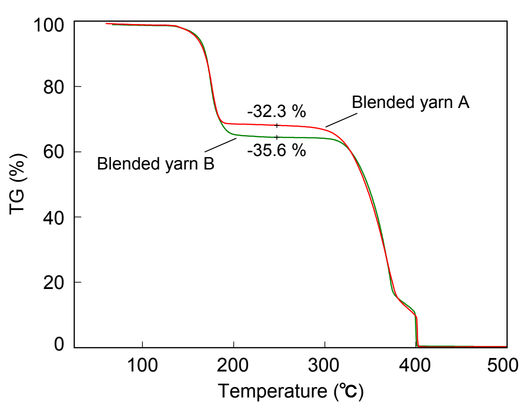

Fig.5 Conversion results of TG curves for the blended yarn A and B
Heating rate : Converted to 0.1 ℃/min from 10 ℃/min
: Blended yarn A, polyester : cotton = 67.3 : 32.7
: Blended yarn B, polyester : cotton = 65.1 : 34.9

Thermo Gravimetry / Differential Thermal Analyzer
TG/DTA7200
(SII NanoTechnology Inc.)

The TG curves for the blended yarns are shown in Figure 4. A two stage weight decrease was observed for both blended yarns A and B between 300 and 400 ℃, bordering at around 330 ℃. The first weight decrease up to around 330 ℃ was due to the decomposition of cotton and the second weight decrease was due to polyester. The ratio of these weight decreases can determine the cotton/polyester ratio of the blended yarns. However, it is difficult to accurately read the weight decrease ratios from the results in Figure 4 and clarify the difference since the blend ratios differ by only 2%.

Heating Rate Conversion Simulation Method was used to convert the blended yarns A and B measurement results of Figure 4 to data of a heating rate of 0.1 ℃/min. Figure 5 shows the results. The two-stage weight decrease was completely separated for both blended yarns. The first-stage weight decrease rates, which equates to the thermal decomposition of cotton, for blended yarns A and B were 32.3% and 35.6% respectively. These results clearly define the difference between blended yarns A and B.

CONCLUSION

Heating Rate Conversion Simulation Method can clearly distinguish cotton/polyester blend rates of down to difference of 2 %. While it would require over 3 days to actually measure at a heating rate of 0.1 ℃/min to 500 ℃, This method can perform low-heating measurement simulations in a short amount of time. Heating Rate Conversion Simulation Method can clearly separate multiple weight decreases that occur in the same temperature region. It is expected to be applied to various fields.