Application News

IRTracer™-100 Fourier Transform Infrared Spectrophotometer

Real-Time Measurement of Thermal Curing Reaction of Automotive Paint Using FTIR

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User Benefits

- Effective curing conditions for CO_2 reduction can be determined by real-time measurement of the thermal curing reaction of paints.
- The heated ATR accessory used in this measurement enables measurements in the temperature zone from room temperature to 130 °C.
- In the single-reflection ATR method, measurement is possible with one drop of specimen material due to the small size of the ATR prism.

■ Introduction

Various countries and regions are promoting in a wide range of initiatives for introduction of renewable energy and reduction of CO_2 emissions with the aim of achieving carbon neutrality by 2050 (the Chinese government plans to achieve net-zero carbon by 2060). Focusing on the automobile industry, which is a particularly large source of CO_2 emissions, because approximately 25 % of CO_2 emissions in the manufacturing process occur in the coating film forming process [1], auto makers and paint makers are developing new paints for CO_2 reduction in that process. In the coating film forming process, after the paint is applied, it is dried by baking at a high temperature to thermally cure the paint. However, shortening the paint curing time and curing at lower temperatures are considered to be effective measures for reducing CO_2 emissions.

In this article, the thermal curing reaction of paint was measured in real time by using an FTIR and a heated ATR accessory. The structures of paint change partially in the thermal curing reaction, hence the optimum curing conditions can be determined by focusing on the peaks of the functional groups originating from the changed structures. Here, an acrylic urethane paint used in automobiles was measured.

IRTracer™-100 MicromATR

Fig. 2 Appearance of Instruments

Table 1 Measurement Conditions

Instruments	: IRTracer-100 MicromATR (diamond single-reflection heated disk with temperature controller)
Resolution	: 4 cm^{-1}
Accumulation	: 20 times
Wavenumber range	: 4000 - 400 cm^{-1}
Apodization function	: Happ-Genzel
Detector	: DLATGS

■ Thermal Curing Reaction of Acrylic Urethane Paint

One type of paint which is used in automobiles is acrylic urethane paint. The main agent in this paint is acrylic polyol, and an aliphatic polyisocyanate is used as the curing agent. A polymerization reaction begins when these two liquids are mixed, and urethane bonds are formed. Fig. 1 shows the reaction formula. Acrylic urethane paint is a strong, tough paint with weathering resistance and gasoline resistance. Its drying time is longer than that of other lacquer paints, but can be shortened by heating.

-R-COO-R'-OH + O=C=N-R'' = -R-COO-R'-O-C(=O)-N(H)-R''

Acrylic polyol (main agent) | Isocyanate (curing agent) | Acrylic urethane resin

Fig. 1 Reaction Formula of Acrylic Urethane Resin

■ Analysis Conditions

The measurement was carried out using an IRTracer-100 Fourier transform infrared spectrophotometer (FTIR) and a MicromATR heated-type single-reflection attenuated total reflection (ATR) accessory. Fig. 2 shows the appearance of the instruments, and Table 1 shows the measurement conditions. The measurement was carried out in the MicromATR while heating the sample with an ATR heating disk. The heated disk of the MicromATR used in this measurement enables measurements in the temperature zone from room temperature to 130 °C.

■ Sample Preparation

A commercially-available acrylic urethane paint was used in the measurement. The main agent and curing agent were mixed at a ratio of 10 : 1, and after stirring well, one drop of the paint was deposited on the prism of the ATR and measured.

■ Change of Spectrum Before/After Curing

Fig. 3 shows the overlay of the spectrum before curing, which was measured immediately after mixing the main agent and the curing agent, and the spectrum measured after the paint was allowed to cure completely by holding at room temperature for 3 days after mixing.

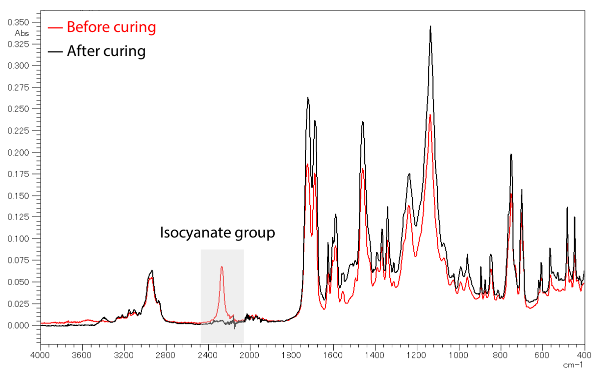

Fig. 3 Spectra Before/After Paint Curing

In the spectrum before curing, the peak of isocyanate group contained in the curing agent can be observed at around 2270 cm^{-1}, but the isocyanate group cannot be seen after curing, suggesting that information concerning curing can be obtained by focusing on the isocyanate group.

Measurement of Time Course in Paint Curing Reaction

After mixing the main agent and the curing agent of the paint, a 2-hour time course was measured at various constant temperatures, and the reaction rate D_R was calculated from the measured spectra. Here, the reaction rate D_R was calculated by the following mathematical expressions, after first calculating the peak intensity A_{NCO} originating from the isocyanate group at around 2270 cm^{-1} normalized based on the peak intensity A_{CH3} originating from the methyl group at around 2940 cm^{-1}, which does not change before and after curing (see Fig. 4) [2].

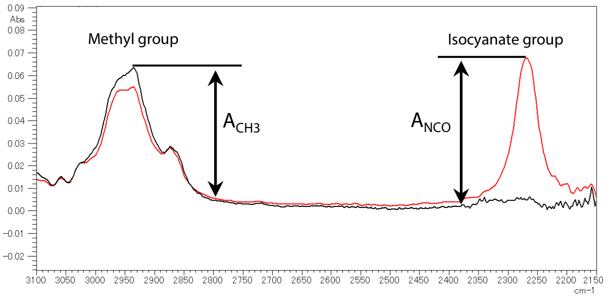

Fig. 4 Enlargement of 3100 to 2150 cm^{-1} Wavenumber Range in Fig. 3

$$R(t) = A_{NCO}(t)/A_{CH3}(t)$$

$$D_R = 1 - R(t)/R(0)$$

- t : thermal curing time
- $A_{NCO}(t)$: peak intensity at around 2270 cm^{-1} at thermal curing time t
- $A_{CH3}(t)$: peak intensity at around 2940 cm^{-1} at thermal curing time t
- R(t) : peak intensity ratio of isocyanate group and methyl group at thermal curing time t
- D_R : reaction rate of polymerization reaction

Fig. 5 shows the calculated reaction rate D_R plotted against the thermal curing time t. Because the reaction rate D_R approaches 1 as thermal curing proceeds, it is possible to estimate the effective conditions for the thermal reaction of the paint from Fig. 5.

From Fig. 5, it is clear that thermal curing proceeds rapidly at the set temperatures of 80 °C and 100 °C, as a reaction rate D_R of approximately 0.8 was achieved with both temperatures 30 minutes after the start of curing. However, the thermal curing temperature of 80 °C is more suitable than 100 °C from the viewpoint of CO_2 reduction. As reference, at the set temperatures of 60 °C and 40 °C, it was found that D_R was less than 0.7 even after 2 hours, and additional time would be necessary for complete curing.

Conclusion

The thermal curing reaction of paint was measured in real time by using an FTIR and heated ATR accessory. Thermal curing of the acrylic urethane paint used in this measurement proceeded more rapidly as the temperature increased, but no change could be seen in the thermal curing reaction speed at temperatures higher than 80 °C. Therefore, it can be inferred that the most suitable thermal curing temperature is 80 °C.

As shown by this experiment, it is possible to estimate the optimum thermal curing temperature and time by tracking the thermal curing reaction in real time.

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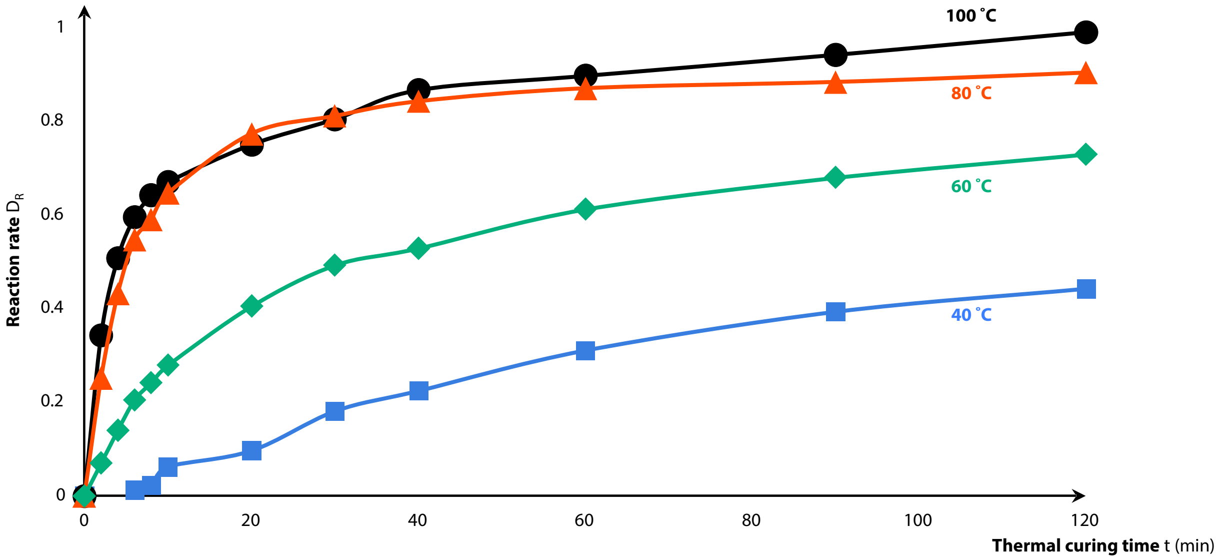

Fig. 5 Relationship of Reaction Rate D_R and Thermal Curing Time t at Various Constant Temperatures