

Study of Curing Behavior of Urethane Clear for Short Baking

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ABSTRACT

Curing behavior required for polishing repair of the clearcoat has been studied with the aim of shortening the baking time for reducing CO₂ emissions in the coating process. The authors also studied curing behavior that enables the transition of Isocyanate to the basecoat from the clearcoat.

As a result, it was found that polishing reparability is enhanced by increasing the storage modulus of the clearcoat at the end of baking. Furthermore, it was found that there is a correlation between the time until the storage modulus rises and transition amount of isocyanate to the basecoat. The curing behavior required for a shorter baking time and directivity in resin design were determined from these results.

1. Introduction

At Honda, development into reducing volatile organic compounds and dechlorination has been conducted for the purpose of decreasing the amount of environmentally hazardous substances used in automobile coating⁽¹⁾. In recent years, amidst a strong demand for the reduction of greenhouse gas emissions that are said to cause climate change, the reduction of CO₂ emitted in automobile manufacturing processes has become an important issue.

In the body coating process at automobile manufacturers, a 3-coat 2-bake coating system with shorter processes has been developed for reducing CO₂ emissions⁽²⁾⁻⁽¹⁰⁾. On the other hand, although a 3-coat 1-bake coating system is being introduced in bumper coating ahead of body coating, further reduction of CO₂ emissions is required.

Shortening of the baking time is effective for reducing CO₂ emissions that are generated in the bumper coating baking process. During the baking process, it is important that coating performance, such as mechanical strength and chemical durability, is contributed to by crosslinking of the clearcoat and control of transition of curing components between coats. Conventional methods where crosslinking of coats after baking is analyzed is limited to qualitatively ascertaining curing behavior during the baking process, and quantitative analysis of coating performance was not possible. For this reason it is considered that, by quantitatively analyzing curing behavior in the baking process to clarify the correlation with coating performance,

the optimum curing behavior can be established to further shorten the baking time.

This paper describes the results of analyzing the relationship between curing behavior and coating performance in the clearcoat baking process that is required to achieve a shorter baking time.

2. Issues in Shortening the Baking Time

Clearcoat that is used on resin parts including bumpers is a two-portion-type urethane resin made up of hydroxy-containing acryl and a hexamethylene diisocyanate trimer (isocyanurate trimer) on the curing component. In the coating process, this coat is a low-viscosity fluid that can be easily handled, whereas in the baking process, the coat is a thermosetting resin material that becomes a rigid coated film as a result of a three-dimensional crosslinking structure that forms due to a crosslinking reaction. To shorten the baking time, it is important that polishing reparability after baking and coating adhesion in the user's operating environment be satisfied after having promoted the crosslinking reaction between the acrylic resin and isocyanate.

The coat structure on the bumper is as follows. A clearcoat is a multilayer film formed on the basecoat by recoating as shown in Fig. 1, and the bumper coat has a mechanism where a crosslinking reaction occurs on the basecoat during baking by isocyanate transiting to the basecoat from the clearcoat after coating clearcoat and, as a result, coat strength is enhanced and film adhesion

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properties are expressed.

A coated film that satisfies coating performance, such as polishing reparability and film adhesion properties can be obtained by performing baking of this coat at 80°C for 20 minutes.

A common method for shortening the baking time is to add a curing-acceleration catalyst such as dibutyltin dilaurate (DBTDL) to the clearcoat to promote the reaction⁽¹¹⁾. It is known that polishing reparability during baking is enhanced by promoting the crosslinking reaction of the clearcoat by this method. On the other hand, because the crosslinking reaction of the clearcoat is promoted, the transition amount of isocyanate to the basecoat decreases, raising the issue that adhesion will drop. For this reason, the clarification of the relationship between curing behavior and coated film performance in the baking process and the setting of an optimum curing behavior become issues.

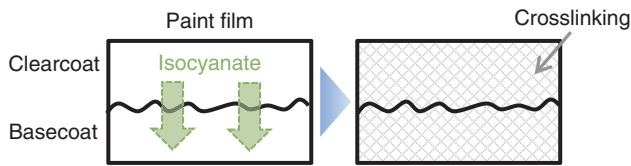


Fig. 1 Film structure of automotive bumper paint

3. Approach to Ascertaining Curing Behavior

With the crosslinking reaction in the baking process, it is presumed that functional groups that should react are already in pairs as shown in Fig. 2 and will not react by a typical 2-component reaction, and that these are connected as a stochastic process. It is considered that a pair of specific functional groups is formed because the crosslinking structure restricts motion⁽¹²⁾.

In the reaction shown in Fig. 2, in which specific functional groups AB react to link together, the formation speed of reaction product AB is expressed as $k \text{AB}$ (where, k is the reaction rate constant). Loss of AB is proportional to time t , and the 1st-order reaction rate equation in Eq. (1) is derived if the product after all AB pairs react is taken to be $AB(\infty)$ and the start time of the 1st-order reaction is taken to be td .

$$AB = AB(\infty)\{1 - \exp[-k(t - td)]\} \quad (1)$$

To ascertain the curing behavior in the baking process, measurement of changes in the crosslink density during curing is necessary. The crosslink density is reflected as the storage modulus since, in almost all cases, the coat state during curing is in the rubber elastic region⁽¹³⁾. For this reason, the curing behavior in the baking process can be ascertained by measurement of changes in the storage

modulus during curing.

A rigid-body pendulum-type physical properties testing instrument (RPT-3000W made by A&D Company Limited) as shown in Fig. 3 was used to track changes in the storage modulus during the baking process. This instrument allows a pendulum supported on its knife-edge as its reference point to freely swing in contact with a coating film, and calculates changes in the storage modulus of the coating film from the measured cycle. The swing cycle of the pendulum changes due to changes in dynamic properties when a clearcoat is present between the substrate and knife-edge in the state as shown in Fig. 3. Relative storage modulus $E'r$ can be found as Eq. (2) from the swing cycle of the pendulum⁽¹⁴⁾.

$$E'r = (1/T^2 - 1/T_0^2)/(1/T_1^2 - 1/T_0^2) \quad (2)$$

T_0 : Swing cycle without coating film

T_1 : Swing cycle at reference point

T : Swing cycle with coating film

If Eq. (1) is applied to changes in $E'r$, Eq. (1) can be considered to conform with the test equation that is equivalent to the 1st-order reaction rate equation shown in Eq. (3) from the time that the gelation reaction concludes onwards.

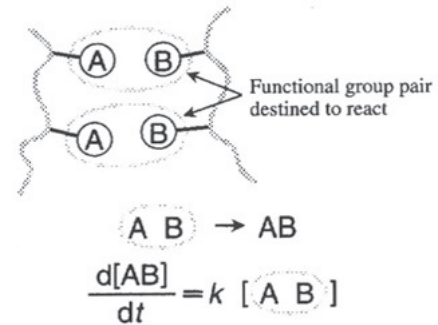


Fig. 2 Hypothetical 1st order reaction. Concentration of reaction product $[AB]$ increases in exponential function.

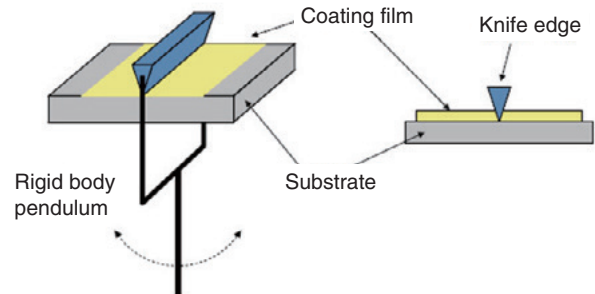


Fig. 3 Rheological measurement apparatus

$$E'r = E'r(\infty)\{1 - \exp[-k(t - td)]\} \quad (3)$$

t : time [min]

$E'r(\infty)$, k , td : constant

It was confirmed that, in curing processing, $E'r$ is proportional to the crosslink density within the limits of changes in $E'r$ that conform to the 1st-order reaction equation⁽¹⁵⁾.

In this study, verification of the correlation with the 1st-order reaction equation will be performed to confirm whether the curing behavior of the coating film can also be tracked by using $E'r$ in bumper coating. The purpose of this study is to clarify the relationship between curing behavior and coating performance, as well as to construct a curing behavior concept with a view to shortening the baking time.

4. Test Methods

4.1. Specimen Preparation Method

The sample for measuring curing behavior was prepared by coating a 0.5 mm-thick stainless steel substrate with clearcoat to a film thickness of 30 μm after baking. The temperature rise curve was set so that temperature rose from 25°C to 80°C in 15 minutes after which the baking temperature was maintained at 80°C or 90°C at 10 or 20 minutes.

The sample for confirmation of polishing reparability and film adhesion properties was prepared by coating priming paint on a polypropylene substrate and further applying a black basecoat, on top of which was applied a prepared clearcoat, and then baking for 10 or 20 minutes at 80°C.

The sample for verification of the transition amount of isocyanate was prepared by coating a black basecoat on a polypropylene substrate, then a prepared clearcoat, baking for 10 or 20 minutes at 80°C, and then peeling off the coated film from the polypropylene substrate to isolate the coated films.

4.2. Polishing Reparability Test Method

Testing of the polishing repair was performed 10 minutes after baking and removal of the sample prepared in Section 4.1. above. After polishing for 15 seconds with 2500 grade sandpaper with a load of 600 g applied, it was confirmed that polishing reparability was possible without any occurrence of white blurs as shown in Fig. 4.

4.3. Film Adhesion Properties Test Method

Film adhesion properties were tested according to a cross-cut test method (JIS K5600)⁽¹⁶⁾ in which a test piece is immersed in 40°C water for a specified period of time and then removed, and the test piece then checked for occurrence of swelling, peeling, etc. of the coated film.

4.4. Transition Amount of Isocyanate Verification Method

The rear surface of the basecoat of the coated film was

measured by a Fourier transform infrared spectrophotometer (Nicolet iS10 FT-IR made by Thermo SCIENTIFIC), and the ratio between the peak intensities of nurate ring derived from isocyanate (1690 cm^{-1}) and ester derived from acrylic resin in the basecoat (1730 cm^{-1}) was measured based on the chart shown in Fig. 5. The calibration curve of the nurate ring/ester peak intensity ratio (1690 cm^{-1} /1730 cm^{-1}) against the amount of isocyanate blended in the basecoat was used to calculate the amount of isocyanate contained in 1 cm^3 of basecoat resin component according to Eq. (4).

$$\begin{aligned} \text{Transition amount} \\ \text{of isocyanate} \\ (\text{cm}^3/\text{Resin cm}^3) \end{aligned} = \frac{\text{Isocyanate} \\ \text{transferred (cm}^3\text{)}}{\text{Resin component} \\ \text{added with transferred} \\ \text{isocyanate (cm}^3\text{)}} \quad (4)$$

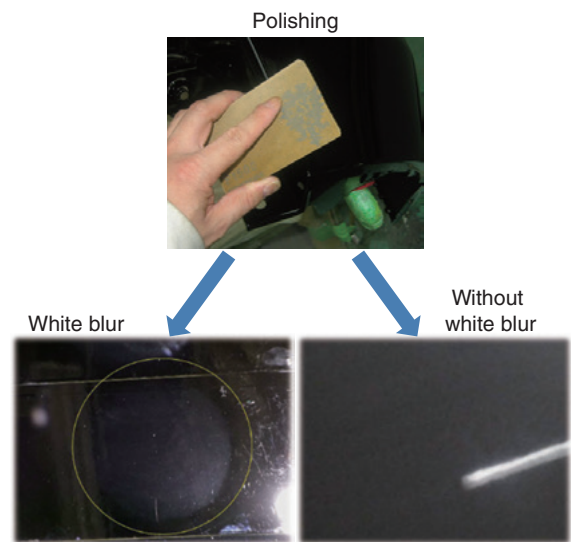


Fig. 4 Schematic diagram of repairability test

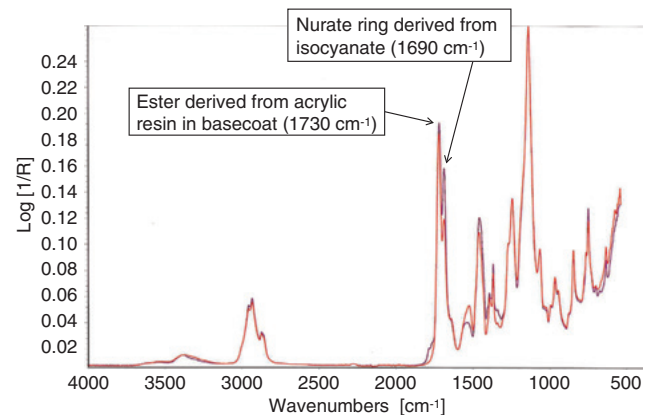


Fig. 5 FT-IR chart of basecoat film

5. Testing and Verification of Curing Behavior and Observations

5.1. Relationship Between Curing Behavior of $E'r$ in Curing Processing and 1st-order Reaction Rate Equation

Figure 6 shows the result of evaluating the relationship between change in behavior of $E'r$ in the baking process and the 1st-order reaction rate Eq. (3) by using 80°C baking-type clearcoat that forms a urethane bond made up of hydroxy-containing acrylic resin that is used in bumpers and isocyanate.

$E'r$ resulted in approaching a coefficient of multiple correlation of 0.999 with respect to the 1st-order reaction rate Eq. (3) within a baking time of 25 to 60 minutes. From this fact, it was confirmed that even with the 80°C baking-type clearcoat that was used in this study, $E'r$ indicates changes in the storage modulus in the curing process, and that use of $E'r$ enables tracking of the curing behavior.

5.2. Result of Influence of Increase in Catalyst Amount on Polishing Repairability and Film Adhesion

Table 1 shows the result of having verified polishing repairability and adhesion properties by conventional clearcoat and by a model clearcoat whose catalyst amount has been increased to twice the conventional amount. When the baking time was reduced simply with a conventional clearcoat, the crosslinking reaction of the clearcoat would not progress sufficiently, resulting in both polishing repairability and film adhesion properties being lowered. When the amount of catalyst added to the clearcoat is excessively increased, however, it was found that the crosslinking reaction progresses at the same rate as in the current reaction and polishing repairability is enhanced although adhesion deteriorates.

Figure 7 shows the result of the transition amount of isocyanate at this time. A decrease in the transition amount

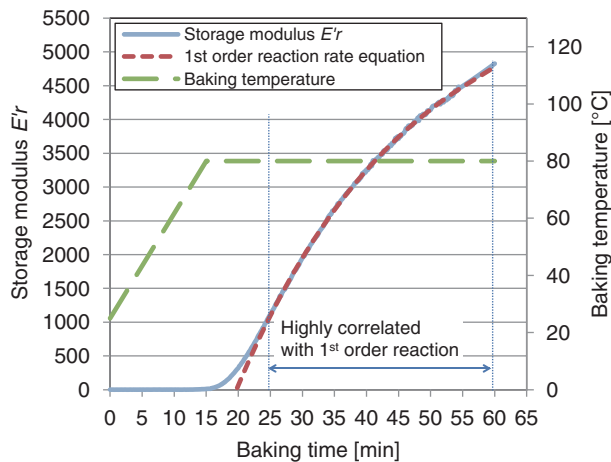


Fig. 6 Storage modulus behavior and 1st order reaction rate equation in baking process

Table 1 Result of spot repair and adhesion property

	Baking condition	Polish	Adhesion	Test number
Current clearcoat	Standard 80°C 20 min	Good	Good	(1)
	Shortened 80°C 10 min	Poor	Poor	–
Current clearcoat with double catalyst		Good	Poor	(2)

of isocyanate to the rear side of the basecoat could be confirmed by doubling the conventional amount of catalyst used.

Whereas the crosslinking reaction of the clearcoat was promoted by an increase in the amount of catalyst added to the clearcoat, and polishing repairability was enhanced as anticipated, it is considered that promotion of the crosslinking reaction in the clearcoat suppresses the transition of isocyanate to the basecoat, resulting in peeling of the coated film.

From these results, it was considered to be important to clarify the curing behavior at the end of baking of the clearcoat that is required for satisfying polishing repairability as well as to clarify the curing behavior of the baking process that is required in transition of isocyanate to the basecoat.

5.3. Verification Result of Polishing Repairability and $E'r$ at Completion of Baking

Figure 8 shows the results of verifying the relationship between polishing repairability and $E'r$ after baking has elapsed by using a conventional clearcoat and a clearcoat

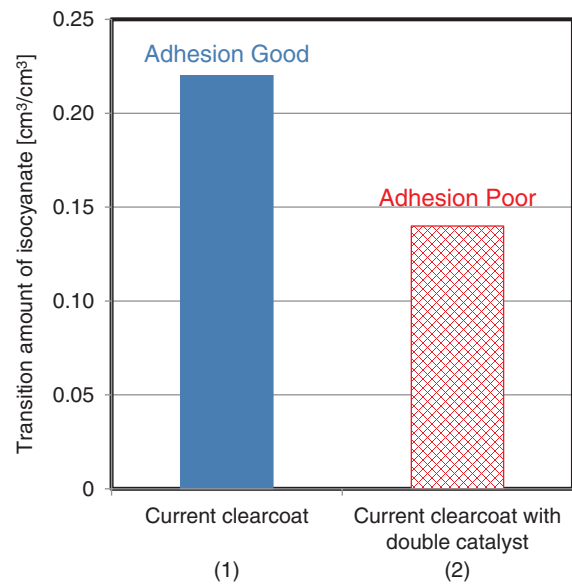


Fig. 7 Transition amount of isocyanate at increasing amount of catalyst

whose catalyst amount has been increased to twice the conventional amount.

The value immediately after baking ends at fixed baking conditions is used for $E'r$ at the completion of baking.

It was found that all coats satisfy polishing repairability at an $E'r$ of 2500 or higher. It is considered that, along with lengthening of the baking time, each of the functional groups of hydroxy-containing acrylic resin and isocyanate form a sufficient crosslink, and that the storage modulus of the coated film increases, which results in formation of a clearcoat having satisfactory polishing repairability. Generally, it is considered that the apparent crosslink density at the end of baking can be increased by increasing molecular weight, glass transition temperature, and the amount of functional groups as coating resin properties.

5.4. Verification Results of Transition Amount of Isocyanate and $E'r$ Rise Start Time

Figure 9 shows the results of having prepared a model clearcoat whose curing catalyst amount has been increased from 0.5 times to twice the amount, and having verified the relationship between the transition amount of isocyanate to the basecoat and the $E'r$ rise start time and coating adhesion. The time from start of baking until $E'r$ reaches 5 is used for the $E'r$ rise start time to clarify the time it takes for the affect of measurement noise to be eliminated and for temperature rise to begin.

It was found that the transition amount of isocyanate to the basecoat increases and adhesion is enhanced by delaying the time until $E'r$ rises.

It was also found that the time until $E'r$ rises speeds up and, at the same time, the transition amount of isocyanate increases by baking at 90°C compared with baking at 80°C. It is considered that solvent volatility was promoted the higher the baking temperature became, the time until $E'r$ rises increased, and, at the same time, the drop in the

coated film melting viscosity due to the rise in coated film temperature promoted the transition of isocyanate to the basecoat. Although increasing the baking temperature to 90°C cannot be considered as a countermeasure for CO₂ emissions since this increase leads to an increase in CO₂ emissions, which is contrary to the original purpose of this study, it became clear that the same trend was present even at different temperatures. Generally, it is considered that initial curing of baking can be delayed by lowering molecular weight, glass transition temperature, and the amount of functional groups as coating resin properties.

5.5. Observations Intended for Shortening Baking Time

Figure 10 shows the concept behind shortening the baking process based on the above results. To satisfy

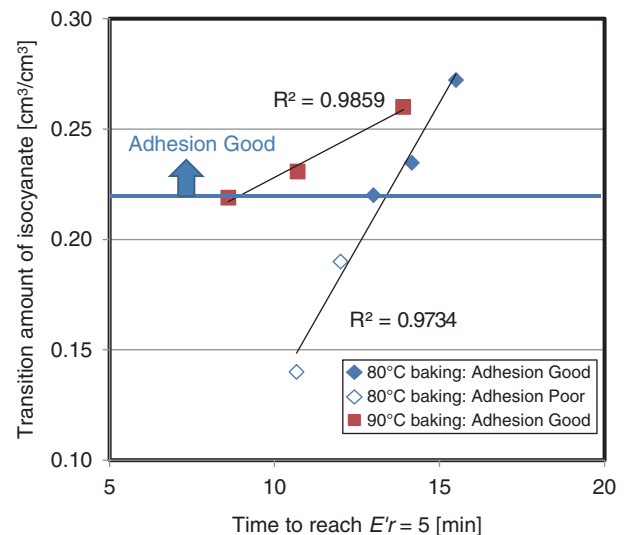


Fig. 9 Relationship between time to reach $E'r = 5$ and transition amount of isocyanate

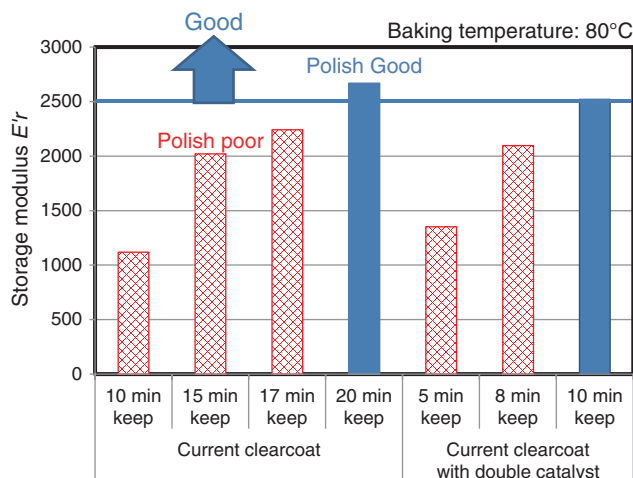


Fig. 8 Relationship between sharpness and storage modulus

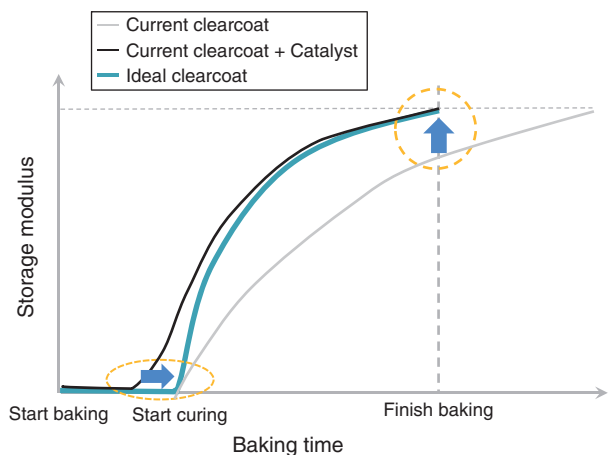


Fig. 10 Concept of storage modulus for short baking clearcoat

polishing repairability, it was considered that increasing $E'r$ at the end of baking was necessary for increasing the storage modulus by the crosslinking reaction caused by baking. On the other hand, to satisfy film adhesion, it was considered that delaying the time until $E'r$ starts to rise was necessary for maintaining required isocyanate transition. These are considered attainable by altering curing properties in the initial and later stages of baking by combining resins having slow and fast curing speeds by the design of molecular weight, glass transition temperature, and the amount of functional groups as coating resin properties.

6. Conclusion

Regarding the curing behavior during baking of clearcoat that is required to shorten the baking process, our study focused on the relationship between polishing repairability and film adhesion after baking. The following results were obtained through this study.

- (1) Even with 80°C baking-type clearcoats, it has been confirmed that $E'r$ in the baking process approaches a coefficient of multiple correlation of 0.999 with respect to the 1st-order reaction rate equation, and curing behavior can be traced.
- (2) To satisfy polishing repairability, $E'r$ in the final stage of baking should be increased.
- (3) To satisfy film adhesion, the time until $E'r$ rises should be delayed and the transition amount of the curing agent to the basecoat should be increased.

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