ALSTECC PROGRAM: CHARACTARIZATION OF A SHORT CYCLE RTM FOR MASS PRODUCTION

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Keywords: *Short Cycle RTM, Rapid Cure Resin, Rapid Impregnation, Automobile.*

Abstract

Two innovative technologies, "Rapid cure resin" and "Rapid impregnation method" have been developed. Rapid cure resin achieved 3 min resin flow and total 5 min resin cure at same temperature. Rapid impregnation method achieved 2.5 min impregnation into dry fabric. These technologies have enabled short cycle RTM, only 10 min molding. Composites using the short cycle RTM have acceptable mechanical properties for automobile parts and application of the method to an actual door inner panel was demonstrated.

1 Background

A strong demand for improving a fuel consumption of automobiles, which eventually contributes to reduce green house gas (CO_2) emission and to prevent global warming, is existed. For automobiles, the energy required for production is in a 1 to 9 ratio to the energy required for driver usage. Thus improved mileage is effective for reducing green house gas. Lighter bodies of automobiles are thought to be the trump of this improved mileage. Some automotive parts have been converted from conventional steel to high strength steel or aluminum. Moreover, a carbon fiber reinforced plastics (CFRP), whose strength is higher than high tensile steel, are being considered as the automotive structures among automakers.

CFRP is currently the center of attention as the lightest materials. But, on the point of economy, mass production technology and assembly processing technology, there have been many difficult problems that should be solved early.

In such situation, a material, composite parts manufacturer (Toray) and an automaker (Nissan) are directly cooperated and started "Automobile Lightweight Structural Elements of CFRP Composites (ALSTECC) program" in Japan. This is a 5-years government program (NEDO) since October 2003. This purposes is development of mass production technologies and design technologies of CFRP for automobile body-in-white (BIW) made with continuous carbon fiber [1][2].

Two innovative technologies of "Rapid Cure Resin" and "Rapid Impregnation Method" were developed in this program. These technologies have been integrated and achieved a short cycle RTM only in 10min. The short cycle RTM is assumed to enabled to a large parts of automobile body production at the rate of 30,000 units per year as shown in Fig. 1. In this paper, the 10min molding demonstration applied to 3D-shape door inner panel and the basic study of short cycle RTM are reported.

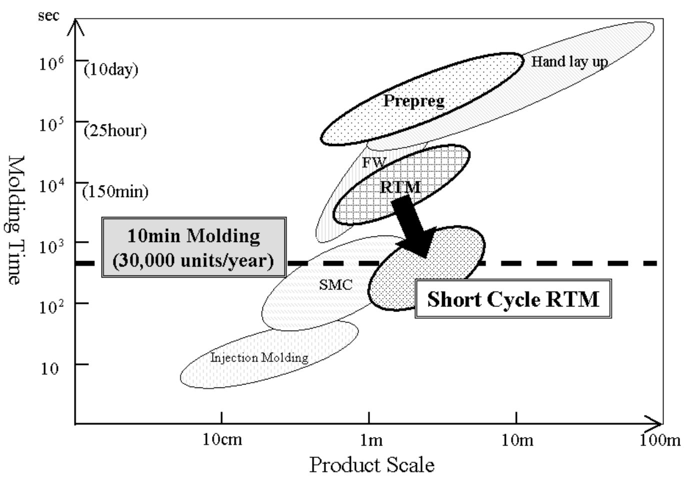

Fig. 1 Target of Short cycle RTM.

2 Introduction of our short cycle RTM

As shown in Fig. 2, conventional RTM had taken a long time to achieve both appearance quality and mechanical properties. Now, the two innovative technologies shorten the RTM cycle dramatically.

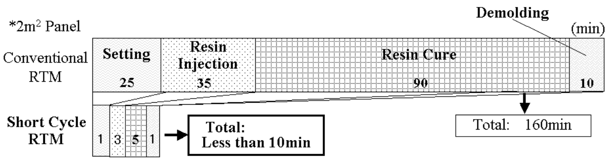

Fig. 2. Time apportion of RTM molding process.

The first technology was rapid cure resin. RTM is a molding method that resin impregnates into dry fabric. In RTM resin, low viscosity under 300 mPa・s and long pot life to flow through dry fabric is required for easy impregnation. Amine cure epoxy resin was conventionally used for RTM resin, because of high mechanical properties. To achieve its long pot life, its resin cure time also became long as shown in Fig. 3. An anionic polymerization with a chain transfer agent achieved a breakthrough in resin curing. This cure sequence enabled to keep low viscosity in 3min, which was enough time to flow through dry fabric, and to cure rapidly in only following 2min without raising temperature [3][4].

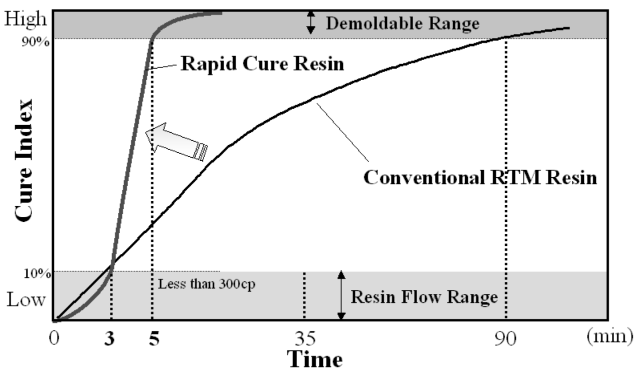

Fig. 3. Concept of the rapid cure resin.

Second technology was rapid impregnation method. For excellent performance of the rapid cure resin, resin injection time could be shortened less than its resin flow time in 3min. As shown in Fig. 4, conventional RTM injection method that made the resin flows from one side to another side in surface took long time because of high fluid resistance in the dry fabric and long flow distance. The flow resistance variation makes it difficult for the controlled impregnation. Furthermore, non-impregnation spots were easily generated based on conventional method, since resin flows faster through the edge parts of fabric where fluid resistance was very low. Flow time based on this method depends on size of products. To achieve 3min-impregnation for large-scale structures such as BIW, completely different method had been required. Proposed rapid impregnation method could solve these difficult problems. According to this method, the resin was injected immediately from multi-gate located above the dry fabric, and the resin flow could be controlled though the fabric thickness direction. As a result, the flows through the edge of fabric are prevented in early stage of injection. Finally this new method achieved 2.5min-impregnation without non-impregnation spots [5].

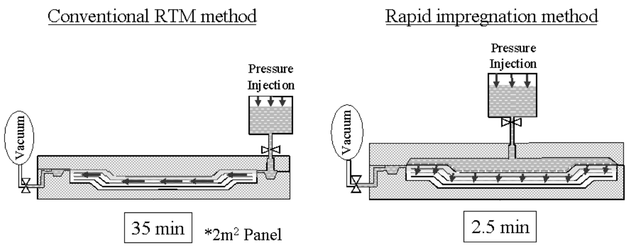

Fig. 4. Schematic of two resin injection methods.

3 Material properties and resin flow simulation of the short cycle RTM

3.1 Mechanical properties of rapid cure resin

Database of the rapid cure neat resin and CFRP made by RTM have been constructed as shown Table 1 and 2. CFRP specimens (about 2t) were made with the dry fabric and the rapid cure resin by RTM. As the dry fabric, plain weave fabric “CO6343B” (T300-3K, 198g/m^2, Toray Industries) were stacked for 9 ply in the same direction 0-90º. The mechanical properties were almost equivalent to that of the conventional RTM resin and CFRP with it, which indicates CFRP with the rapid cure resin was appropriate for automobile structural parts.

Table 1. Mechanical properties of rapid cure resin.

Resin		Conventional Resin for RTM	Rapid Cure Resin
Cure mechanism		Amine Cure	Anionic Polymerization with a Chain Transfer Agent
Tg	℃	110	125
Tensile Strength	MPa	84	79
Tensile Modulus	GPa	3.3	3.5
Elongation	%	5.7	5
Flexure Strength	MPa	147	136
Flexure Modulus	GPa	3.1	3.3
Water Absorption	%	1.7	3.1
Viscosity at 100℃	mPa･s	12	17

Table 2. Mechanical properties of CFRP.

Resin		Conventional Resin	Rapid Cure Resin
Tg	ºC	108	116
Tensile Strength	MPa	684	676
Tensile Modulus	GPa	68	68
Compression Strength	MPa	610	620

*Vf60% conversion

3.2 Effects of weld line

Mechanical properties of CFRP (continuous carbon fiber reinforced) at weld line were evaluated. The multi-gate injection is likely to generate weld lines where resins from different gates meet each other in continuous carbon fiber. Generally, decline of mechanical properties at the weld lines was serious on discontinuous fiber reinforced thermoplastic resin injection molding.

Three kinds of CFRP (about 2t, Vf= 53%) plates were made with the dry fabric and rapid cure resin by RTM. As the dry fabric, plain weave fabric "BT70-30" (T700S-12K, 315g/m^2, Toray Industries) were stacked for 7 ply in the same direction 0-90º. On the first type plate "Blank" that was not including weld lines, resin flow was controlled in one way from injection gate to outlet. On the second type plate "Co-injection", the resin was injected from two gates diagonally located on the tool at the same time to meet resin in line. This type plate was reproduction of the practical RTM applied with multi-gate injection. On the third type plate "Co-cure", the first resin was injected from one gate and stopped injecting at the time about half area of the dry fabric was impregnated.

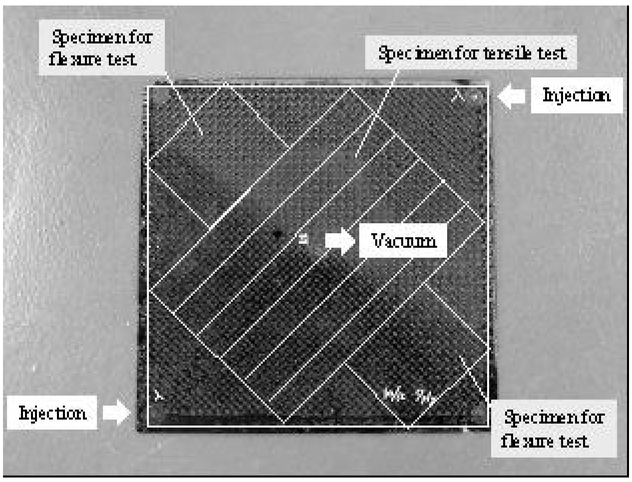

Fig. 5. Weld line and cut-pattern of specimens.

When the first resin was cured, the second resin was injected to impregnate residual half area of the dry fabric from another injection gate diagonally located on the tool. Because the first resin injected from the 1st gate had already been cured, there must be generated weld line when the second resin injected from the 2nd gate met it. Consequently, the specimens including weld line could be made. It is thought that "Co-cure" is worst case in RTM method.

Before testings with aforementioned coupons, two resins were colored to different color to confirm the location that the resins met. Each resin was injected from two gates diagonally located on the tool. The different colored resins met in line and dummy weld line was seen. The specimens for tensile and flexure were cut from each plate as shown in Fig. 5.

The results are shown in Table 3 and 4. In case of tensile testing, significant difference among three kinds of plates has not been observed if the specimen included weld line or not. But in case of flexure testing that was affected by the resin properties, "Co-cure" shows lower strength. On the other hand, "Co-injection" has not been declined both in tensile and flexure testing. Consequently, the test realized multi-gate injection didn't affect the mechanical properties of CFRP. Also, in the worst case that weld line is generated, the mechanical properties of "Co-cure" shows still high and it can be applied to automobile structural parts even if CFRP includes weld line. This high weld line property is thought to be contribution of continuous fiber reinforcement.

Table 3. Tensile properties of CFRP.

		Blank	Coinjection	Co-cure
Tensile Strength	MPa	1217	1228	1187
cv.	%	7	4	6
Tensile Modulus	GPa	71	71	69
cv.	%	3	1	2

Table 4. Flexure properties of CFRP.

		Blank	Coinjection	Co-cure
Flexure Strength	MPa	952	1012	854
cv.	%	10	7	7
Flexure Modulus	GPa	57	59	53
cv.	%	2	3	4

3.3 Quantification for flow properties of fabric

To simulate the resin flow through the dry fabric, speed of resin impregnation was evaluated based on experiments. In these experiments, an impregnation coefficient that was unique to each fabric was derived from Darcy's law. It was revealed that the impregnation coefficient was a dominant factor of the resin flow on the rapid impregnation method.

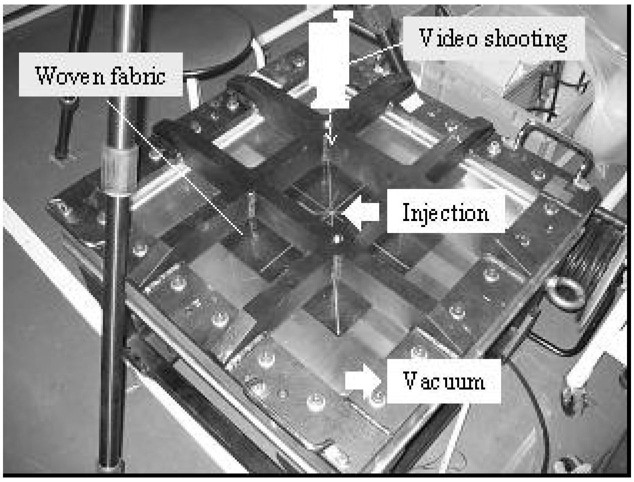

Fig. 6. Tool for radial flow test.

There are some test methods for measuring impregnation coefficient. For example, in rectilinear flow test, one-dimensional flow on the rectangular tool was observed and impregnation coefficient is calculated from flow distance-time relation. In this project, radial flow test that was suited to a reproduction of multi-gate injection has been done as shown in Fig. 6. Specifically, resin was injected from central gate immediately below the dry fabric and the tool cavity was vacuumed from outlet located around the fabric. Lid was made of transparent acrylic to observe the resin flow during the testing. An oil solution that has no reactivity and was similar to the rapid cure resin in its viscosity (10 mPa·s), was applied instead of the resin. In radial flow test, two-dimensional flow like a disk was observed and impregnation coefficient from the relation between the radius of the flow front and time was evaluated.

To calculate impregnation coefficient, analytic equation is led by arrangement below with use of law of mass conservation (Eq. 1) and Darcy Law (Eq. 2). Now, the expression of u is fluid velocity, K is impregnation coefficient, μ is viscosity, and P is pressure.

$$\nabla \cdot u = 0 \tag{1}$$

$$u = -\frac{K}{\mu} \cdot \nabla P \tag{2}$$

When Eq. 1 and Eq. 2 unite, Eq. 3 is led.

$$\Delta P = 0 \tag{3}$$

Because the resin flow is assumed to be isotropic Eq. 3 can be converted into cylinder coordinate system ($(x, y) \rightarrow (r, \theta)$). Impregnation distance is expressed flow front radius r. Pressure gradient should not be occurred in the direction of θ and Eq. 4 is defined with only r.

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)P = \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}\right)P = 0$$

$$\frac{d^2P}{dr^2} + \frac{1}{r}\frac{dP}{dr} = 0 \tag{4}$$

Pressure gradient is assumed to be Eq. 5 with use of constant C and integrated. Now, the suffix of *inj* expresses injection gate and *ff* expresses flow front.

$$\frac{dP}{dr} = -\frac{C}{r} \tag{5}$$

$$\int_{r_{inj}}^{r} \frac{dP}{dr} dr = \int_{r_{inj}}^{r} \left(-\frac{C}{r}\right) dr$$

Eq. 6 is led with use of boundary condition of $P = P_{inj} : r = r_{inj}$.

$$P - P_{inj} = -C \ln\left(\frac{r}{r_{inj}}\right) \tag{6}$$

Also, Eq. 7 is led with use of boundary condition of $P = 0 : r = r_{ff}$.

$$C = \frac{P_{inj}}{\ln\left(\frac{r_{ff}}{r_{inj}}\right)} \quad (7)$$

When Eq. 6 and Eq. 7 unite, Eq. 3 is led.

$$\frac{P}{P_{inj}} = 1 - \frac{\ln\left(\frac{r}{r_{inj}}\right)}{\ln\left(\frac{r_{ff}}{r_{inj}}\right)} \quad (8)$$

On the other hand, when Eq. 2 of Darcy law is arranged with r, Eq. 9 is led.

$$\frac{dr}{dt} = u_r = -\frac{K}{\mu}\frac{dP}{dr} \quad (9)$$

When Eq. 8 is assigned to Eq. 9, Eq. 10 is led.

$$\frac{dr}{dt} = \frac{KP_{inj}}{\mu r \ln\left(\frac{r_{ff}}{r_{inj}}\right)} \quad (10)$$

Eq. 10 can be converted to Eq. 11 by paying attention to the movement of the flow front radius r_{ff}.

$$\frac{dr_{ff}}{dt} = \frac{KP_{inj}}{\mu r_{ff} \ln\left(\frac{r_{ff}}{r_{inj}}\right)}$$

↓ Time integration
(Viscosity is assumed to be constant)

$$\frac{\mu}{KP_{inj}}\int_{r_{inj}}^{r_{ff|t}} r_{ff} \ln\left(\frac{r_{ff}}{r_{inj}}\right) dr_{ff}$$

$$= \int_{r_{inj}}^{r_{ff|t}} \frac{dt}{dr_{ff}} dr_{ff} = \int_0^t dt$$

$$t = \frac{\mu}{KP_{inj}}\int_{r_{inj}}^{r_{ff|t}} r_{ff} \ln\left(\frac{r_{ff}}{r_{inj}}\right) dr_{ff}$$

$$= \frac{\mu}{KP_{inj}}\left(\left[\frac{r_{ff}^2}{2}\ln\left(\frac{r_{ff}}{r_{inj}}\right)\right]_{r_{inj}}^{r_{ff|t}} - \int_{r_{inj}}^{r_{ff|t}} \frac{r_{ff}}{2} dr_{ff}\right)$$

$$= \frac{\mu}{2KP_{inj}}\left[r_{ff|t}^2 \ln\left(\frac{r_{ff|t}}{r_{inj}}\right) - \frac{1}{2}\left(r_{ff|t}^2 - r_{inj}^2\right)\right] \quad (11)$$

When Eq. 11 is arranged with impregnation coefficient K, Eq. 12 is led.

$$K = \frac{\mu}{2P_{inj}t}\left[r_{ff|t}^2 \ln\left(\frac{r_{ff|t}}{r_{inj}}\right) - \frac{1}{2}\left(r_{ff|t}^2 - r_{inj}^2\right)\right] \quad (12)$$

Resin viscosity μ, injection pressure P_{inj}, injection gate radius r_{inj}, and flow front radius $r_{ff|t}$ on the injection time t, can be measured from radial flow test and impregnation coefficient K can be calculated by assigning these parameters to Eq. 12. While viscosity of resin generally becomes high during impregnation, this analytic equation assumes that viscosity is constant. But, it seems to be no problem because the concept of rapid impregnation is to achieve very short injection time.

The specification of the radial flow test actually done is shown below. Flow front radius in 8 direction (0^o, 45^o, 90^o, 135^o, 180^o, -135^o, -90^o, -45 ^{o}) were measured at specified time intervals to take movie using video. Properties of fabric that was applied in the test are shown in table 5. Both of them were plain weave and strand width of fabric A was more than that of fabric B. These fabric were stacked for a specified number of ply in the same direction 0-90^o. The test specifications and results are shown in table 6. Fabric variation and Vf were changed. The test tool cavity thickness was set to 2.4mm constant and Vf was controlled with the number of ply. Impregnation coefficient $K_{0\text{-}90}$ is arranged as the average in the direction of 0^o, 90^o, 180^o, -90^o, $K_{\pm 45}$ is arranged as the average in the direction of 45^o, 135^o, -135^o, -45^o, and K is arranged as the average in all direction after specified time.

One example of the relation between flow front radius and time, between impregnation coefficient K

and time is shown in Fig. 7 and 8. According to Fig. 7, the resin flow is almost isotropic even if there is anisotropic flow in the microscopic area, so multi-gate injection could be designed with isotropic impregnation coefficient.

Table 5. Fabric properties for radial flow test.

Fabric			CF type	Areal Weight[g/m^2]
A	BT70-30	plain weave	T700S-12K	315
B	CO6644B	plain weave	T300-6K	317

Table 6. Test specifications and results for radial flow test.

ID	Fabric	ply	Vf[%]	$K_{0\text{-}90}$[m^2]	$K_{\pm45}$[m^2]	K[m^2]
1	A	6	43.8	1.5E-10	1.2E-10	1.0E-10
2	A	7	51.0	2.1E-11	1.6E-11	1.6E-11
3	A	7	51.0	2.9E-11	2.1E-11	2.0E-11
4	A	7	51.0	4.0E-11	1.5E-11	3.3E-11
5	A	7	51.0	1.8E-11	1.2E-11	1.2E-11
6	A	8	58.3	1.7E-11	6.9E-12	3.5E-12
7	B	6	45.0	4.1E-11	3.7E-11	4.2E-11
8	B	7	52.5	2.0E-11	2.0E-11	1.8E-11
9	B	7	52.5	6.7E-12	7.5E-12	6.9E-12
10	B	8	60.0	6.9E-12	6.3E-12	5.9E-12

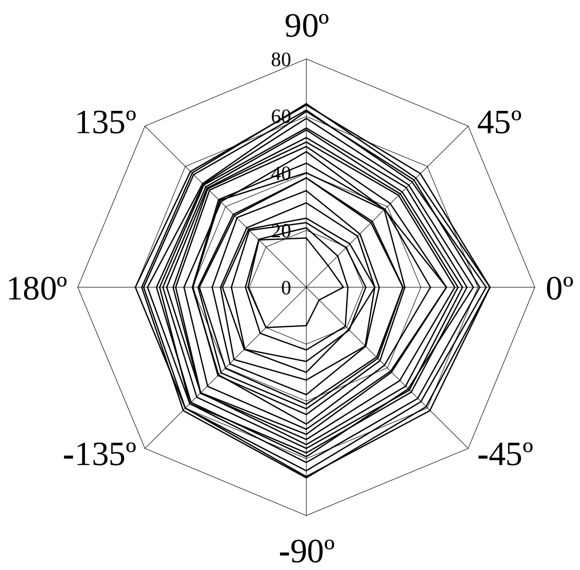

Fig. 7. Flow front radius during 21 sec (ID2). (Each contour line corresponds every sec.)

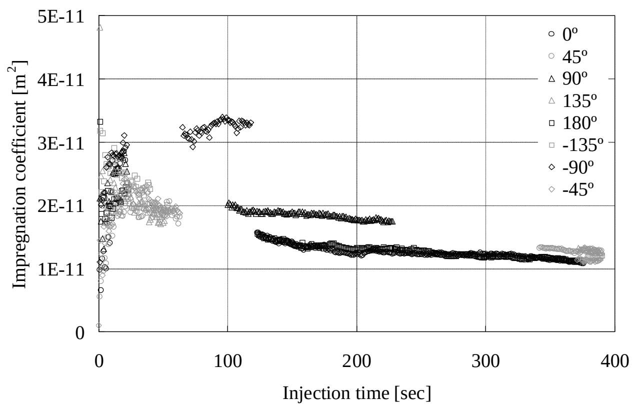

Fig. 8. Shift of impregnation coefficient *K* (ID2).

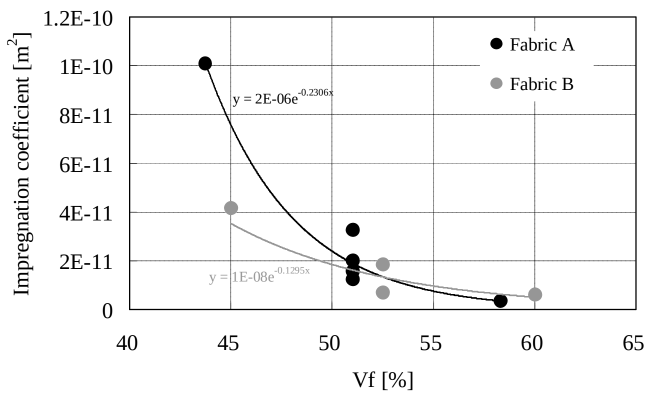

Fig. 9. Relation between Vf and *K*.

In Fig. 8, some data were lacked because resin flow couldn’t be seen because stiffeners of the tool interrupted. Impregnation coefficient *K* varies greatly because pressure is easily changed immediately after injection, but the coefficient *K* stabilized after specified time.

The relation between Vf and impregnation coefficient *K* is shown in Fig. 9. There was good relation, but the relation was changed when the fabric was changed. Not only Vf but also distribution of space affected the resistance of the resin flow and impregnation coefficient *K* including these influence.

3.4 Fluid simulation of multi-gate injection

Based on selecting appropriate impregnation coefficient *K*, the resin flow simulation was conducted with an impregnation simulation software “VaRTIMON” (Toray Industries). Fig. 10 shows a simulation result of conventional RTM at specified time. According to the simulation, almost all of area has not impregnated. On the other hand, Fig. 11 shows a simulation result of multi-gate injection at the same time as Fig. 10. On the other hand, all area has been seen that impregnation was finished. These simulations realized how multi-gate injection is effective for large-scale structure.

On the basis of this simulation, multi-gate injection tool has been optimized and made to demonstrate short cycle RTM.

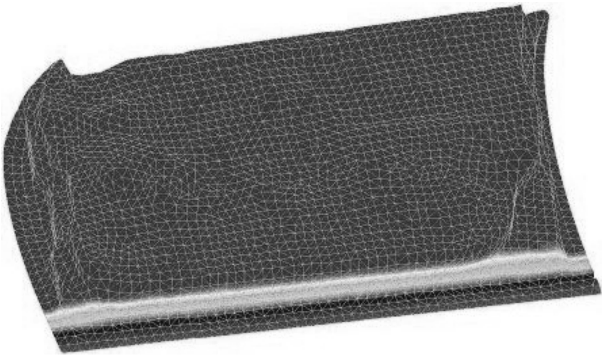

Fig. 10. Simulation result of conventional RTM.

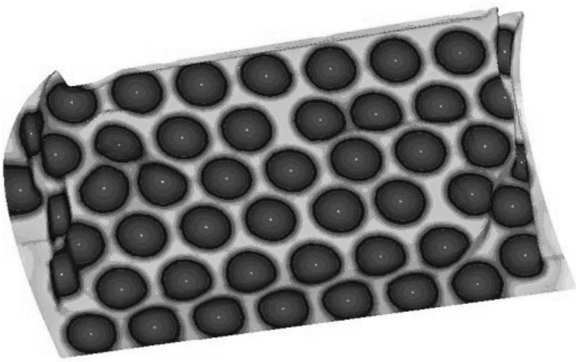

Fig. 11. Simulation result of multi-gate injection.

4 Demonstration of short cycle RTM

Fig. 12. Demonstration of short cycle RTM in 10min.

The two innovative technologies have been successfully integrated and allowed the 10min molding demonstration applied to 3D-shape door inner panel. Fig. 12 shows the CFRP door inner panel fabricated in the demonstration. From this demonstration, the rapid impregnation method can be applied even large-scale structures. Also, the simulation results are in excellent agreement with the demonstration.

5 Concluding remark

Two innovative technologies, “Rapid cure resin” and “Rapid impregnation method” have been developed. Rapid cure resin achieved 3 min resin flow and total 5 min resin cure at same temperature. Rapid impregnation method achieved 2.5 min impregnation into dry fabric. These technologies have enabled short cycle RTM, only 10 min molding. CFRP using the short cycle RTM have acceptable mechanical properties for automobile parts and application of the method to an actual door inner panel was demonstrated.

Acknowledgements

This R&D has been conducted as the part of “ALSTECC Program” supported by NEDO. The authors would like to thank Nissan Motor Co., Ltd., universities partners for their technical contributions.

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