DEVELOPMENT OF ACRYLATE RESIN FOR CARBON FIBER REINFORCED PLASTICS

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Abstract

Carbon fiber reinforced plastics (CFRP) are more and more widely used in civil aircraft. The weight savings they provide make them very attractive for major structural components such as fuselage and wing. Epoxy resin is mainly used for them because it has good mechanical and thermal properties.

We have been developing acrylate resins applied for matrix resins of CFRP suitable for components of aircraft. Acrylate resin is cured by radical chain polymerization. Therefore, it could be cured during a shorter time than conventional epoxy resin cured by step polymerization.

In this study, a new acrylate resin suitable for components of aircraft has been developed. It has enough viscosity suitable for manufacturing prepregs. Nevertheless, it could be cured by ultraviolet light and showed appropriate glass transition temperature. CFRP with this new acrylate resin also investigated. Its mechanical properties stood comparison with the properties of CFRP with epoxy resin.

1 Introduction

Carbon fiber reinforced plastics (CFRP) are more and more widely used in civil aircraft. The weight savings they provide make them very attractive for major structural components such as fuselage and wing. Epoxy resin is mainly used for them because it has good mechanical and thermal properties. However, it is expensive because it needs an autoclave to mold in a conventional usual method.

Acrylate resin is cured by radical chain polymerization. Therefore, it could be cured during a shorter time than conventional epoxy resin cured by step polymerization. It is likable to reduce cure time of resin because it will contribute to reduce the energy cost. Also it could be cured by ultraviolet (UV) light.

Generally, UV light cure system cannot apply to CFRP molding because carbon fiber shield acrylate resin from UV light. So we have developed acrylate resins to make possible to cure under UV light and suitable for components of aircraft [1][2]. We proposed a new acrylate resin in past study [2]. However, the viscosity of the resin was still low for prepregs.

In this study, a new acrylate resin suitable for components of aircraft has been developed. It has enough viscosity suitable for prepregs. Nevertheless, it could be cured by UV light. And it showed appropriate glass transition temperature. CFRP with the acrylate resin was also investigated. Its mechanical properties stood comparison with the properties of CFRP with epoxy resin.

2 Experimental

2-1. Materials

Several acrylate resins such as multifunctional acrylate resin (R1) and difunctional acrylate resin (R2) were used as matrix resin. And polymer (R3) was also used which had still vinyl group. Irgacure 369 (Ciba Specialty Chemicals) as UV light initiator was used. Perbutyl-Z (Nippon Oil & Fats) was used as thermal initiator.

MR50K (Mitsubishi Rayon Co., Ltd.) carbon fiber was used as reinforced fiber.

2-2. Samples

2-2-1. Matrix resin mixture

Resins were mixed in a glass flask at 120 ℃ temperature. UV light and thermal initiator were dissolved by a mixer. (shown in table 1)

2-2-2. Matrix resin specimen

They were poured between two glass plates and cured by UV light (Fusion F300S, bulb D, distance from bulb was 53 mm, light intensity was 1060 mW/cm^2, 24 times irradiation by 1 m/min.), or cured by heat for 1 hour at 150 ℃ curing method using an oven.

2-2-3. Prepare the prepregs

Matrix resin film was made by film coater on release paper. It was put on a drum. Carbon fiber was wound onto it at a speed of 6 m/min. After that, another resin film was put on carbon fiber and they were pressed by Fusing Press (Asahi Seni Kikai Co., Ltd) 4 times at 60 ℃ and 0.15 MPa. Fiber areal weight and resin content were 185 g/m^2 and 40 wt% respectively.

2-2-4. UV curing method of composites

The unidirectional prepregs were laminated in one direction. The laminates were put between two glass plates. It was put on an aluminum plate and wrapped with the vacuum bag (Fig. 1). It was heated from room temperature to 50 ℃ and hold for 3 hours in an autoclave so as to remove micro air from prepregs . After that it was debagged and cured by UV light (Fusion F300S, bulb D, distance from bulb was 53 mm, light intensity was 1060 mW/cm^2, 24 times irradiation by 1 m/min.),

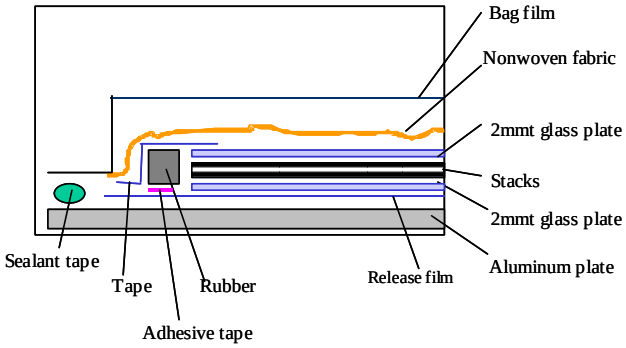

Fig. 1. Cross section picture of vacuum bag method of pre treatment for UV cure molding.

2-2-5. Heat curing method of composites

The unidirectional prepregs were laminated in one direction. The laminates were put on a Aluminum plate and wrapped with the vacuum bag film, heated up from room temperature to 50 ℃ and hold for 3 hours in an autoclave. Then it cured for 1 hour at 150 ℃ (Fig. 2).

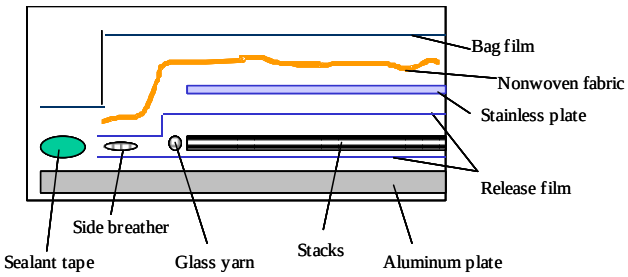

Fig. 2. Cross section picture of vacuum bag method for heat cure molding.

2-3. Measurements

2-3-1. Viscosity

Rheometrics DSR-200 was used to measure viscosity of resin increasing temperature based on ASTM D4473 using 25 mm diameter disposable parallel plates with a gap of 0.5 mm at a frequency of 1 Hz and stress of 30 mN. Ramp rate was 5 ℃ /min.

2-3-2. Dynamic mechanical analysis (DMA)

Rheometrics RDA-700 was used to measure storage modulus (G') increasing temperature based on ASTM D4065.

A specimen was cut to the size of W 12 mm x L 50 mm x T 2 mm from a cured matrix resin panel.

It was measured at a frequency of 1.59 Hz, strain of 0.01 % in resin and 0.05 % in composite and a range of temperature 30 ℃ to 250 ℃. Ramp rate was 2 ℃/min.

G'-Tg was determined by intersection point of two tangent lines for G' before and after G' decreased.

2-3-3. Photo-DSC

TA instruments Q-1000 was used for photo Dynamic Scanning Calorimetry (DSC) of uncured resin.

About 5mg uncured resin was put into an Aluminum hermetic pan. Then the sample resin was irradiated by high-pressure mercury lamp for 0.6 seconds at 30 ℃ after the temperature became stable. The light intensity was 145 mW/cm^2 measured by UNI METER UIT-101 (Ushio Denki Co., Ltd.).

And it was irradiated for 300 seconds for 3 times. It was confirmed that heat flow was no observed.

Then it was irradiated for 0.6 seconds. This sequence was decided as base line.

2-3-4. Three- point bending test

Instron4465 was used for three point bending test.

The cured resin specimens were cut to the size of W 8 mm x L 60 mm x T 2 mm. The test was carried out based on ASTM D790. The cross head speed was 2.0 mm/min. L/D was 16. 6 specimens were tested each.

2-3-5. 0 ° direction Tensile test

Instron4482 was used for 0 ° direction tensile test.

The composite specimens were cut to the size of W 15 mm x L 250 mm x T 1.2 mm. The test was based on ASTM D3039. The glass tabs were used. The number of plies was 6. The cross head speed was 2.0 mm/min. 6 specimens were tested each.

2-3-6. Interlaminar share strength (ILSS) test

Instron4465 was used for interlaminar share strength (ILSS) test. The composite specimens were cut to the size of W 6.35 mm x L 18 mm x T 3 mm. The test was carried out based on ASTM D2344-84. The cross head speed was 1.3 mm/min. L/D was 4. The number of plies was 16. 6 specimens were tested each.

2-3-7. 90 ° direction flexure strength test

Instron4482 was used for 90 ° direction flexure strength test. The composite specimens were cut to the size of W 12.7 mm x L 70 mm x T 3 mm. The test was carried out based on ASTM D790. L/D was 16. The number of plies was 16. 6 specimens were tested each.

3. Results and Discussion

Table 1 shows the mixture ratio of components. Table 2 shows glass-transition temperature of cured resin by DMA. G'-Tg increased in proportion to increasing R1 content ratio.

Table 1. Mixture ratio of components

Resin	A1	A2	A3
R1	0	15	30
R2	100	80	70
Irgacure 369	2	2	2
Perbutyl-Z	3	3	3

(Parts by weight)

Table 2. Dynamic mechanical analysis : Tg Data

	A1	A2	A3
G' -Tg [℃]	128	139	154
tan delta max [℃]	153	164	180

Table 3 shows the mixture ratio of R3 based on A3 resin. The values of uncured resin viscosity and cured resin G'-Tg are shown in table 4. It shows that component R3 contributes to increase the viscosity of resin. It seems that the viscosity of Resin A4 or 5 is suitable for prepregs.

It was ascertained that the cured resin G'-Tg was not affected particularly by R3 content ratio until 30 parts by weight.

It seems that A4 has good balance between viscosity and G'-Tg. A4 was named "H".

Table 3. Mixture ratio of components

Resin	A3	A4	A5
R1	21	21	21
R2	49	49	49
R3	0	30	45
Irgacure 369	2	2	2
Perbutyl-Z	3	3	3

(Parts by weight)

Table 4. Resin properties of A3,4 and 5

Resin	A3	A4	A5
Viscosity [Pa･s]	70	2900	17500
G'- Tg [℃]	154	151	137
tan delta max [℃]	180	177	180

Table 5 shows the viscosity of resin G and H. Resin G is also an acrylate resin developed in the past. Although Resin G could be applied to prepregs, the viscosity of Resin G was still low for it. On the other hand, resin H is much suitable for making prepregs.

Table 5. Resin viscosity of resin G and H

Resin	G	H
Viscosity [Pa･s]	950	2900

Fig. 3 shows photo DSC chart of resin G and H. It means the reactivity by UV light. Both of the resins reacted at almost the same time and the each reaction continued after irradiation. The reaction energy of resin G and H were 59.8 J/g and 42.0 J/g respectively.

Table 6 shows the number of double bond per gram for resin G and H. They were calculated by molecular weight and number of double bond per molecular. The number of double bond of resin H was 80 % of that of resin G. So integrated heat flow could become same percentage logically.

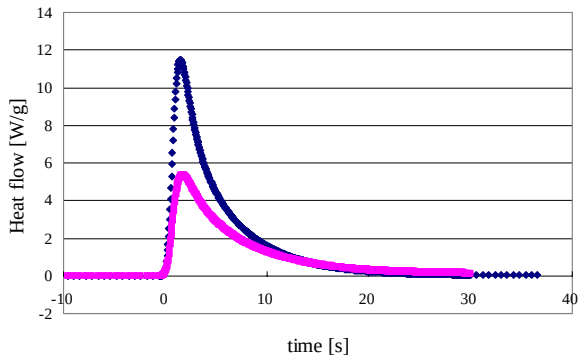

Fig. 3 Photo DSC chart of matrix resin irradiation time 0.6[s] ●:Resin G ▲:Resin H

Table 6. Calculated number of double bond per gram

Resin	G	H
Calculated number of double bond per gram [mol/g]	4.14×10^{-3}	3.35×10^{-3}

However, the reaction energy of Resin H was 70 % of that of resin G. It seems that viscosity would disturb the diffusion velocity of monomer and radical.

Table 7 shows cured resin properties. Resin G and H could be cured by either UV light or heat.

The resin cured by UV light had almost the same mechanical and thermal properties as those of resin cured by heat. Furthermore, resin H had good mechanical properties but they were slightly worse than those of resin G.

Table 7. Cured resin properties

Resin	G		H	
Cure method	UV light	heat	UV light	heat
Flexure strength [MPa]	160	165	140	142
Flexure modulus [GPa]	4.1	4.3	3.9	3.9
Flexure strain [%]	5.1	4.8	4.8	4.4
DMA Tg [℃]	151	159	155	155

Table 8 shows carbon fiber composites properties. Carbon fiber prepregs of Resin G and H could also cured by either UV light or heat. In resin H, the composite cured by UV light had also almost the same mechanical and thermal properties as those of cured by heat. Furthermore, resin H composite had good mechanical properties as compared with those of resin G. The mechanical and thermal properties of them would be suitable for structural components of civil aircraft.

Table 8. Composites properties

Resin	G		H	
Cure method	UV light	heat	UV light	heat
0 ° Tensile strength [MPa]	-	2750	2690	2740
0 ° Tensile modulus [GPa]	-	162	158	164
0 ° Tensile strain [%]	-	1.6	1.6	1.5
90 ° Flexure strength [MPa]	62	64	75	80
90 ° Flexure modulus [GPa]	7.1	8.2	8.2	7.8
90 ° Flexure strain [%]	0.86	0.79	0.64	1.1
ILSS [MPa]	78	90	90	87
DMA Tg [℃]	172	159	152	151

4. Conclusion

We have developing acrylate resins for CFRP. New acrylate resin in this study had suitable viscosity for manufacturing prepregs. The acrylate resin also has good mechanical and thermal properties equal to wide use epoxy resin. It will be appropriate for structural components of civil airplane.

5. Acknowledgment

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6. References

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