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The Influence of Resin Mixture Ratio for the Use of Prepreg on the Fatigue Behavior Properties in FRMLs

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ABSTRACT

Fiber reinforced metal laminates(FRMLs) were new type of hybrid materials. FRMLs consist of high strength metals(Al 5052-H34) and laminated fiber with structural adhesive bond. The effect of resin mixture ratios on the fatigue crack propagation behavior and mechanical properties of aramid fiber reinforced aluminum composites was investigated. The epoxy, diglycidylether of bisphenol A(DGEBA), was cured with methylene dianiline(MDA) with or without an accelerator(K-54). Eight kinds of resin mixture ratio were used for the experiment ; five kinds of FRMLs(1)(mixture of epoxy and curing agent) and three kinds of FRMLs(2)(mixture of epoxy, curing agent and accelerator). The characteristic of fatigue crack propagation behavior and mechanical properties FRMLs(2) shows more effecting than that of FRMLs(1).

Key Words: Fiber Reinforced Metal Laminates(FRMLs), prepreg, matrix resin, curing agent, accelerator, resin mixture ratio, Diglycidylether of Bisphenol A(DGEBA), stress intensity factor(K), fatigue crack growth rate(da/dN), stress intensity factor range(ΔK)

1. Introduction

Composite materials consist of a reinforcement and a matrix resin. Properties of composite materials are explained by the rule of mixture which shows intermediated properties of reinforcement and matrix resin(1,2). However, the rule of mixture is not applied for many cases practically because properties of composite materials are influenced considerable by the interfacial bonding strength of reinforcement and matrix resin(3,4).

The interlaminar of composite materials transmits an external fatigue, a stress and a strain to the fiber, and improves the uniformity and continuity of the reinforcement. Therefore, the mechanical properties of composite materials can be highly enhanced by the improvement of the interfacial bonding strength(5~7).

In this study, the prepreg was manufactured by mixing of the thermosetting epoxy resin(Diglycidylether of bisphenol A type(DGEBA), YD-128, KUKDO Chemical), the curing agent(Methylene dianiline, MDA-150, KUKDO Chemical) and the accelerator (Tris(dimethylamino methyl) phenol, K-54, KUKDO Chemical). There the impregnated unidirectional aramid fiber was wetted by the resin with the variation of the resin mixture ratios. The prepreg of the various the resin mixture ratio was cured between the surface treatment aluminum alloys(Al 5052-H34) using the hot-press.

So, in this paper, the bending strength and the fatigue crack propagation behavior investigated using specimen produced by the process. Particularly, in this experiments, it was investigated of the influences of the resin mixture ratio on the bonding strength, the bending strength and the fatigue crack propagation behavior.

Also, when the ideal equivalence resin mixture ratio of <1:1> is applied the optimal content of accelerator to show the highest adhesive strength was investigated(8,9). The interfacial adhesive strength and the fatigue crack propagation properties with various the resin mixture ratios were examined by the bending test and the fatigue crack propagation test. And then the resin mixture ratio showing the highest mechanical properties was investigated.

2. Experiment

2.1 Manufacture of FRMLs

2.1.1 Manufacture of Prepreg

FRMLs(Fiber Reinforced Metal Laminates) consist of aluminum alloy plate and prepreg generally. Two kinds of prepreg were manufactured with fibers wetted by different resins. The one is made of the unidirectional aramid fiber wetted by the mixture of epoxy resin and curing agent. The other is made of the mixture of epoxy resin, curing agent and accelerator. In the former case, five kinds of the resin mixture ratio were used. In the latter case, three kinds of the resin mixture ratio were used. The reason of using accelerator is for the comparison between the specimen with accelerator and the specimen without accelerator. And the best content of accelerator for the bending strength and the fatigue crack propagation properties are tried to find. The resin made by mixture ratio <1:1> contents of the epoxy and curing agent was modified by accelerator with content 10, 20 and 30 percent.

It is shown in Table 1 of five kinds of the resin mixture ratio of epoxy and curing agent for the manufacture of FRMLs.

The mixture ratio of samples was the volume ratio calculated from the based on the equivalence ratio. According the volume ratio in Table 1, the prepreg was manufactured by unidirectional aramid fiber wetted by resins. And both face of prepreg was sandwiched by laminated aluminum alloy plates(Al 5052-H34) of thickness 0.5 mm. Laminates specimen thickness was 2 mm. This specimens with five kinds of the resin mixture ratio were named as FRMLs(1).

Table 2 displays the resin mixture ratios of the FRMLs(1) with accelerator. The content of accelerator was 10, 20 and 30% of epoxy content. Resin made on the ground of volume ratio was shown in Table 2. Prepreg was manufactured by the unidirectional aramid fiber wetted by the resins. And both face prepreg was sandwiched by aluminum alloy plate(Al 5052-H34) with thickness of 0.5 mm. The laminates specimen thickness was 2 mm. Specimen of three kinds of resin mixture ratios were named as FRMLs(2).

Table 1 The resin mixture ratio system of FRMLs(1)

Factor Name	Component	Epoxy + Curing agent (Equivalence ratio)	Epoxy + Curing agent (Volume ratio#)	Thickness (mm)
FRMLs(1)##	Al 5052 -H34	-	-	0.5
	Prepreg	1 : 0.50	312 : 74.80	1
		1 : 0.75	312 : 112.2	1
		1 : 1.00	312 : 149.6	1
		1 : 1.25	312 : 187.0	1
		1 : 1.50	312 : 224.4	1

Volume ratio = (Molecular weight / Specific gravity) × Equivalence ratio

FRMLs(1) : Fiber Reinforced Metal Laminates(1)

Table 2 The resin mixture ratio system of FRMLs(2)

Factor Name	Component	Epoxy + Curing agent + Accelerator (Equivalence ratio)	Epoxy + Curing agent + Accelerator (Volume ratio)	Thickness (mm)
FRMLs(2)**	Al 5052 -H34	-	-	0.5
	Prepreg	1 : 1 : 0.1*	312 : 149.6 : 37.9	1
		1 : 1 : 0.2*	312 : 149.6 : 75.8	1
		1 : 1 : 0.3*	312 : 149.6 : 113.8	1

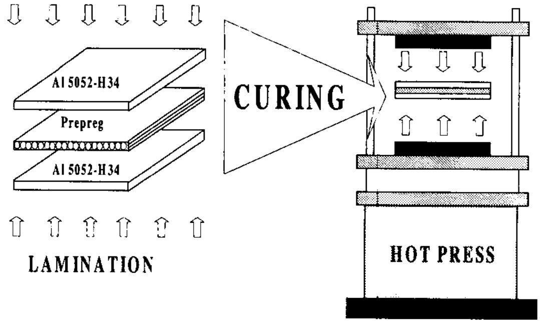
* 10, 20 and 30% of epoxy content

** FRMLs(2) : Fiber Reinforced Metal Laminates(2)

2.1.2 Lamination and Curing

It is shown in Fig. 1 of the laminates type of FRMLs(1) and FRMLs(2) and the curing method. Rolling direction of Al 5052-H34 plate and fiber direction of the unidirectional prepreg in the same direction for the sake of bonding force improvement.

The hot-press for curing is shown in Fig. 1. Artificial bonding there is a deformation on FRMLs because of materials with a different thermal expanse coefficient by curing. In case of laminates of Fig. 1 (a), during a curing, FRMLs should have a residual compressive stress in the prepreg layer and a residual tensile stress in aluminum alloy plates. It is because a fiber will shrink in the fiber direction during cooling from the curing temperature by the reason why existing prepreg is manufactured by B-stage.



(a) Lamination (b) Curing

Fig. 1 Schematic diagram of FRMLs manufacture

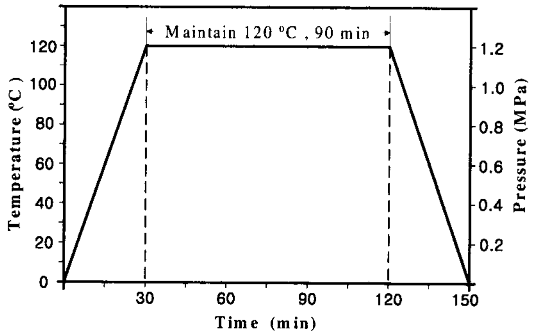


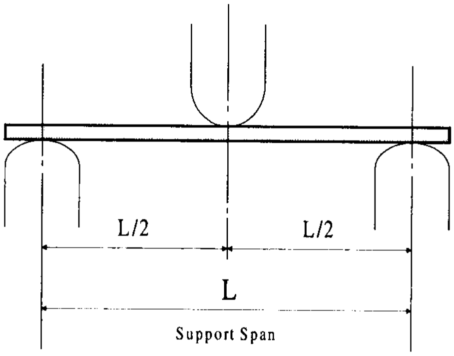
Fig. 2 The curing cycle of FRMLs(1) and FRMLs(2)

Fig. 2 displays the curing cycle applied in FRMLs(1) and FRMLs(2) specimen. The curing temperature was 120℃. The time was 90 minutes, and the pressure was 1.2 MPa. The pre-heating time was 30 minutes and the quenching time was 30 minutes. Therefore a specimen can be made stable chemically.

2.2 3-point bending test

It is shown in Fig. 3 of the 3-point bending test. According to the resin mixture ratio, the maximum bending strength was measured. Moreover, the shearing strength was investigated on the interface of fiber layers and aluminum layers.

This test was performed based on ASTM D 790M-95$^{(10)}$ and an universal testing machine(DDS-10T, Shimadzu Co.) was used.



Note : **Maximum Radius Support = 1.5 Times Specimen Depth**
Maximum Radius Loading Nose = 4 Times Specimen Depth
Nominal Specimen Depth (mm) ; 2
Specimen Width (mm) ; 25
Specimen Length (mm) ; 50
Support Span (mm) ; 32

Fig. 3 Schematic diagram of loading nose and support on 3-point loading

2.3 Fatigue crack propagation test

Fig. 4 displays the CCT(Center Cracked Tension) specimen for the fatigue crack propagation test.

The CCT specimen has an artificial notch of 13.5 mm from the circular hole. Test was performed based on ASTM E 647-95$^{(11)}$. Applied stress was 45 percent of yield stress, 180 MPa of Al 5052-H34 presented in ASTM B 209-95$^{(12)}$. Therefore the maximum stress was 81 MPa the stress ratio was 0.1. And the stress wave form was sinusoidal with 10 Hz.

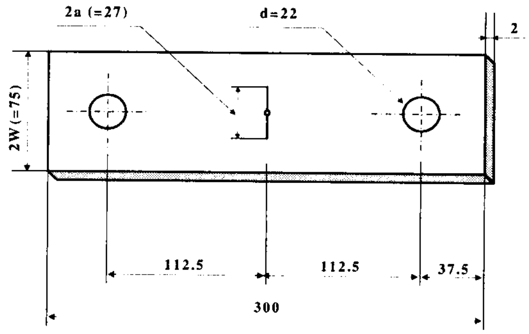


Fig. 4 Shape of CCT specimen (unit : mm)

The stress intensity factor range(Δ K) at crack tip of CCT was calculated by Eq. (1). Where f(a/w) was the geometry factor of CCT specimen(13).

$$\Delta K = f(a/W)\,\Delta\sigma\sqrt{\pi a} \qquad (1)$$

where,

$$f(a/W) = \sqrt{\frac{\pi a}{4W}\sec\frac{\pi a}{2W}}\left[1-0.025\left(\frac{a}{W}\right)^2+0.06\left(\frac{a}{W}\right)^4\right]$$

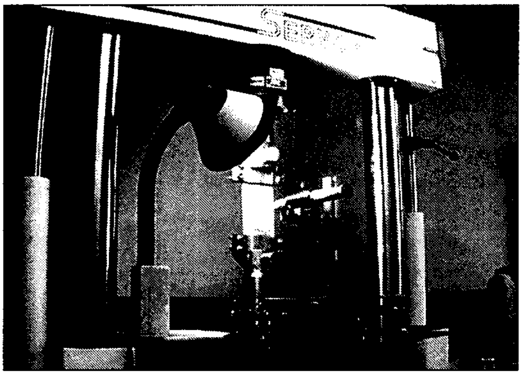


Fig. 5 Equipment and travelling microscope

It is shown in Fig. 5 of grip parts of the fatigue test equipment(EHF-ED 10-20L, Shimadzu Co.) for the fatigue crack propagation test. From the artificial notch the crack length was measured at every 1 × 10^3 cycle using the travelling microscope.

3. Result and discussion

3.1 3-point bending test

It is shown in Fig. 6 of the result of the maximum bending strength with respect to resin mixture ratio.

The maximum bending strength FRMLs(1) shows approximately 2 times improved compare with that of Al 5052-H34 with the same thickness. The maximum bending strength FRMLs(2) shows approximately 2.2 times improved compare with that of Al 5052-H34 with the same thickness. As a result of the bending test, FRMLs(2) with accelerator shows approximately 10% more improved the maximum bending strength than FRMLs(1) without accelerator. Therefore an accelerator improves not only reduction of a manufacture process and a catalytic action of curing but also the mechanical properties of specimen. The maximum bending strength of FRMLs(1) takes place at the resin mixture ratio <1:1>. However the variation of bending strength with respect to the change of accelerator content was not observed.

The maximum bending strength of FRMLs(2) was not proportional to increment of accelerator. When the accelerator content was 20%(<1:1:0.2>), the maximum bending strength was obtained. But when the accelerator content was 30%(<1:1:0.3>), the bending strength decrease with the content. That is to say, the optimal accelerator content is 20% of the epoxy content.

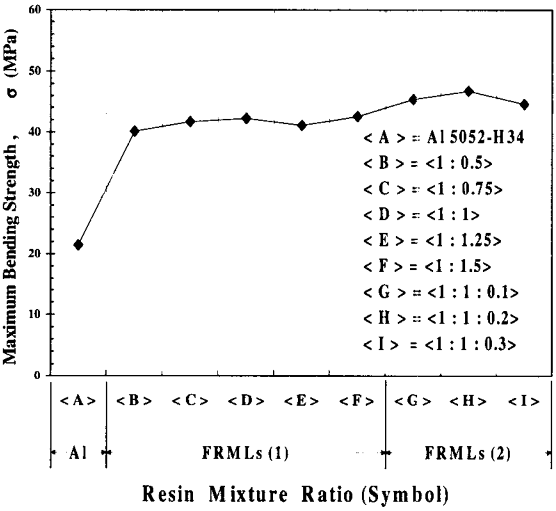


Fig. 6 Result of three-point bending test

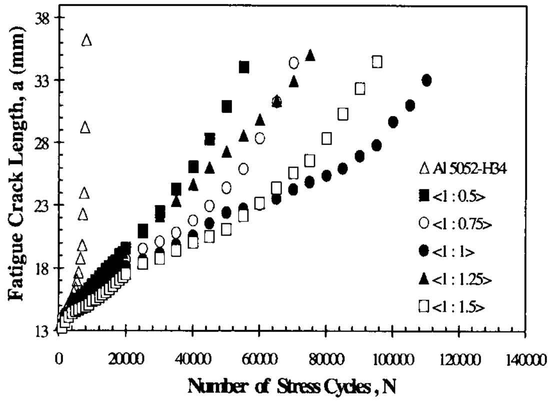
3.2 Fatigue crack propagation test

It is shown in Fig. 7 of the fatigue crack propagation properties versus cycles. In Fig. 7 (a) and (b), the fatigue properties of FRMLs(2) is superior to fatigue properties that of FRMLs(1). For example, in Fig. 7, FRMLs(2) shows improvement of fatigue life 7 times to 14 times longer than Al 5052-H34 with the same thickness. It is because of the crack closure of interlaminar at stronger fiber layer than aluminum layer. Therefore, it is shown that Al 5052-H34 shows fast crack propagation during the regular cycle. Also, fiber layer would not be failed by crack, and the main crack reduce stress intensity factor and COD at crack tip. Therefore crack propagation rate is reduced. This phenomenon is explained by the crack-bridging which causes the crack propagation retardation(14).

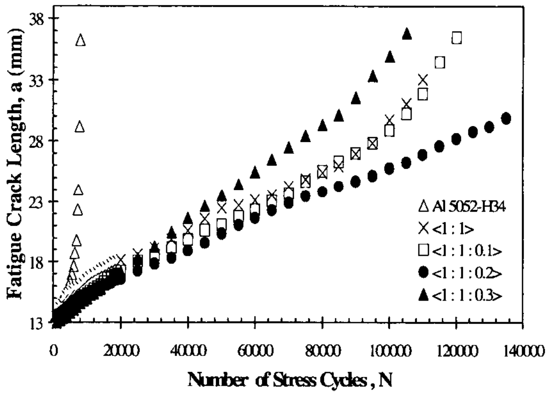
The crack propagation behavior of FRMLs(1) at the resin mixture ratios <1:0.5>, <1:0.75>, <1:1>, <1:1.25> and <1:1.5> shows similar aspect until 2 × 10^4 cycle. However, it appears remarkably different on the crack propagation rate over 3 × 10^4 cycle. On the whole, the resin mixture ratio <1:1> shows extremely superior fatigue life. The resin mixture ratio <1:0.5> shows the shortest fatigue life. Therefore the resin mixture ratio <1:1> and <1:0.5> shows the different fatigue life at approximately 6 × 10^4 cycles. Moreover, Fig. 7 (b) at the resin mixture ratio <1:1:0.1>, <1:1:0.2> and <1:1:0.3> is similar to Fig. 7 (a), but Fig. 7 (b) longer fatigue life than Fig. 7 (a). FRMLs(2), shows the fatigue life approximately 13 times to 18 times longer than Al 5052-H34. In case of FRMLs(2) the crack propagation rate shows divergence over 8 × 10^4 cycles.

The resin mixture ratio <1:1:0.2> shows the most stable crack propagation. Between the resin mixture ratio <1:1:0.2> and <1:1:0.3>, the difference of the fatigue life according to 10% of accelerator content is approximately 4 × 10^4 cycles. Also, because FRMLs(2) is FRMLs(1) containing 10, 20 and 30% accelerator in the resin mixture ratio <1:1>, FRMLs(1) at the resin mixture ratio <1:1> need to be compared with FRMLs(2). The resin mixture ratio <1:1:0.1> shows similar tendency to FRMLs(1) of the resin mixture ratio <1:1>. When the epoxy resin is added by 10% accelerator of content, the increment of fatigue crack propagation properties was not show. But by the addition of accelerator content 20%, the remarkable improvement of fatigue crack propagation properties was shown. When the accelerator is added to 30%, extremely high fatigue crack propagation takes place. Over-hardness is occurred by the mixing of accelerator over 30% most of prepreg curing is done at room temperature in manufacture process of FRMLs(2). Consequently, it is main reason to the decrement of interlaminar force of prepreg and the delamination. The delamination weaken the interlaminar bonding strength by cyclic interlaminar shearing stress around crack, and the effect of crack-bridging mechanism was decreased.

Roebroeks(15) found that the delamination would start at the different distance from a crack tip. Finally, the resin mixture ratio <1:1:0.3> shows noticeable decrement of fatigue life in comparison with the resin mixture ratio <1:1:0.2>.



(a) Al 5052-H34 and FRMLs(1)



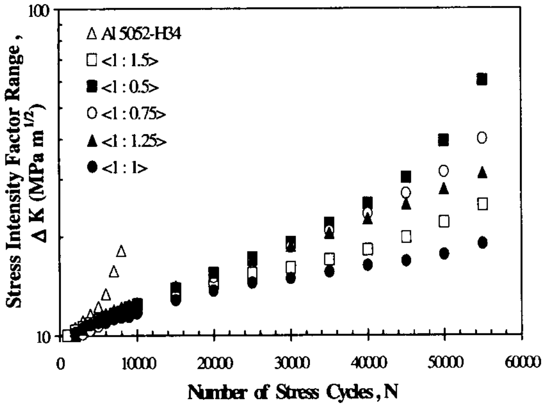
(b) Al 5052-H34 and FRMLs(2)

Fig. 7 Result of fatigue crack propagation test

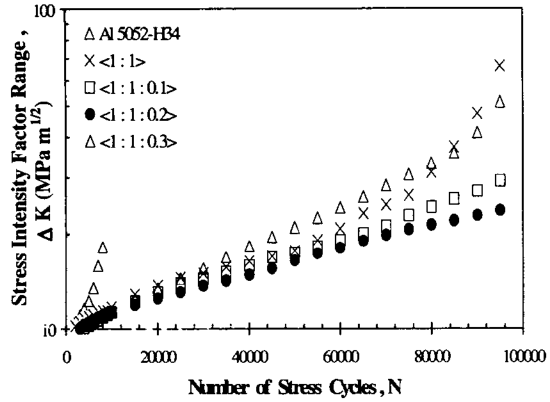
It is shown in Fig. 8 of relation between cycle and the stress intensity factor range. In case of the resin mixture ratio <1:0.5>, <1:0.75> and <1:1.25> in Fig. 8 (a), the stress intensity factor range(Δ K) does not show any difference until 4 × 10^4 cycle. The increment of cycle is proportional to that of the stress intensity factor range(Δ K), and exponentially increases over 5 × 10^4 cycle.

The stress intensity factor range(Δ K) in stress field of crack tip shows the lowest at <1:1>. The difference of stress intensity factor range(Δ K) was 40 MPa· $m^{1/2}$ between the resin mixture ratio <1:1> and the resin mixture ratio <1:0.5>.

In Fig. 8, the difference between resin mixture ratios <1:1:0.1> and <1:1:0.2> makes a little difference of ΔK than Fig. 8 (a). Therefore, it is found that FRMLs(2) shows the superior properties of fracture toughness than FRMLs(1).



(a) Al 5052-H34 and FRMLs(1)

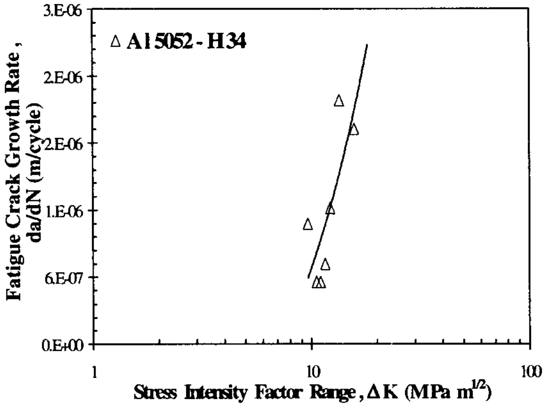


(b) Al 5052-H34 and FRMLs(2)

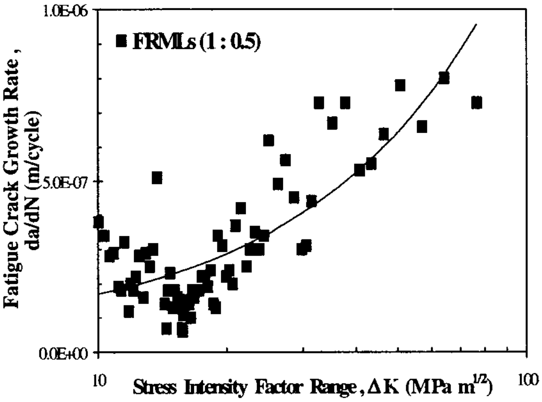
Fig. 8 Result of relation between ΔK and number of cycles

FRMLs(1) at <1:1> and FRMLs(2) show that the resin mixture ratio <1:1> and <1:1:0.1> have similar tendencies of Fig. 7 (b). Over 5×10^4 cycle, the slope of <1:1> becomes steeper than that of <1:1:0.1> as cycle increases. As a result, it is known that the accelerator acts as a decreasing factor of the stress intensity factor range at a crack tip. The increment of interlaminar bonding strength as result of accelerator of optimal contents induced stable crack growth and then increased fatigue life. But, in case of accelerator over additive 30%(<1:1:0.3>), it's a bad influence on fatigue crack propagation properties. Also, ΔK of resin mixture ratio <1:1:0.3> shows more distinguished increment than that of the resin mixture ratio <1:1:0.1> and <1:1:0.2>.

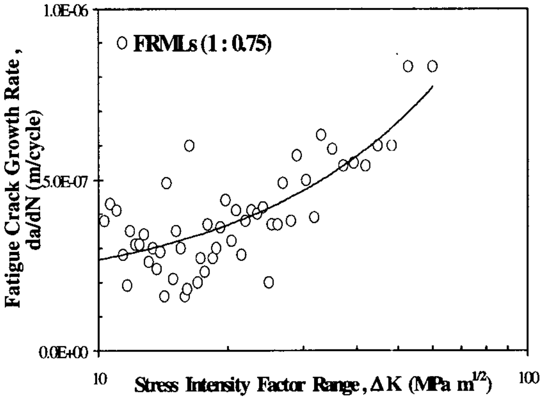
It was shown in Fig. 9 (b), (c), (d), (e) and (f) of relation between the fatigue crack growth rate(da/dN) and the stress intensity factor range(ΔK) at FRMLs(1).



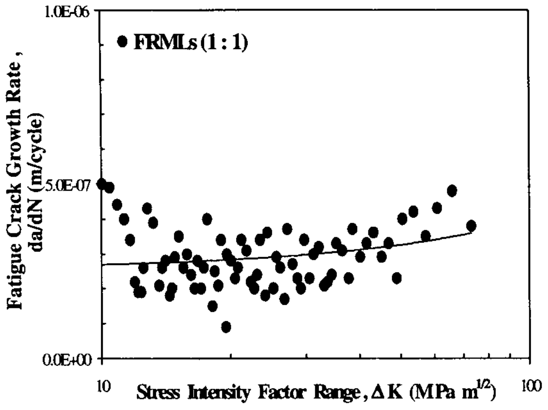
(a) Al 5052-H34



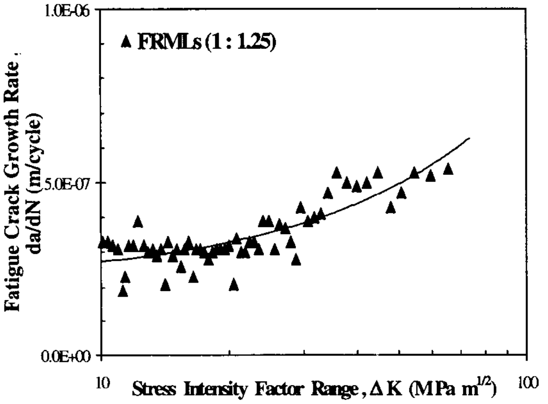
(b) Resin mixture ratio <1:0.5>



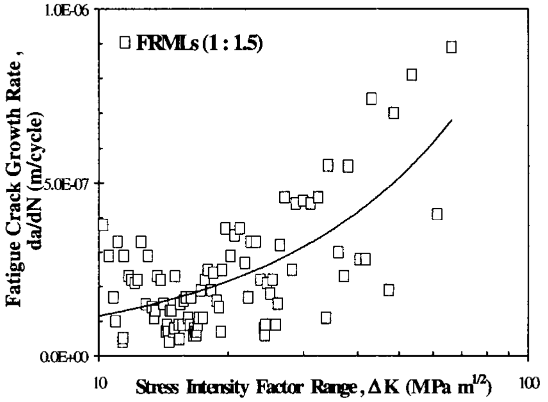
(c) Resin mixture ratio <1:0.75>



(d) Resin mixture ratio <1:1>



(e) Resin mixture ratio <1:1.25>



(f) Resin mixture ratio <1:1.5>

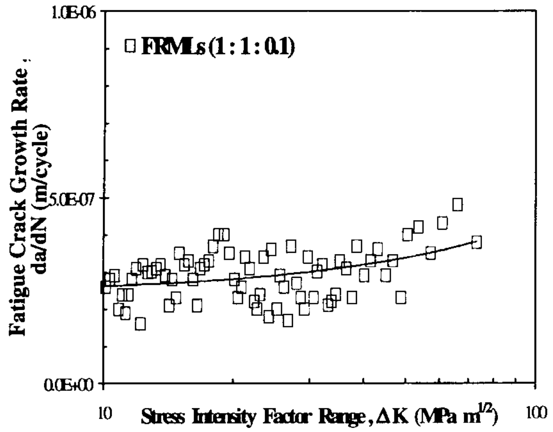
Fig. 9 Relation between fatigue crack growth rate (da/dN) and stress intensity factor range(ΔK) in FRMLs(1)

It is shown in Fig. 9 (a) of a result of fatigue crack growth rate(da/dN) and stress intensity factor range(Δ K) in Al 5052-H34. Data of FRMLs(1) are very scattered. This result is caused by irregular crack propagation rate. Al 5052-H34 shows that crack propagation rate after a accelerating of certain cycles. On the contrary, in case of FRMLs(1) the irregular crack propagation rate have nothing to do with increase of cycles.

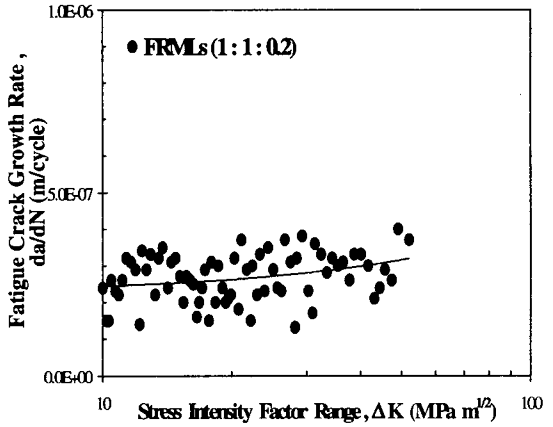
As mentioned above, the irregular crack propagation rate is due to the result from the crack closure and the crack-bridging effect by the fiber layer. The scatter range depends on the resin mixture ratio. Which means that the scatter is correlated with the irregular bonding strength of the fiber layer and the aluminum layer. Namely, energies of specimen transmitted by external force were not reserved as elastic energies through the interlaminar from aluminum layer. Accordingly, in case of unstable interlaminar bonding, energies of specimen transmitted by external force that don't reach the fiber layer are consumed for the crack propagation of the aluminum layer with unstable interlaminar bonding. As crack propagation direction and fiber direction was perpendicular, the crack-bridging effect increases according to interlaminar bonding force. Consequently, the resin mixture ratio <1:1> with the lowest slope is the ideal resin mixture ratio because the accelerator content was a variable of the interlaminar bonding force. In the meantime, aramid fiber and wicked impregnation of epoxy resin was the cause of fiber buckling under the compressive loading(16). Therefore, rapid curing due to too much accelerator causes buckling.

In Fig. 9, low gradient of the crack growth rate means that the crack growth rate doesn't change during the crack growth. When data in Fig. 9 is can be fitted by Paris equation, i. e., $da/dN = C(\Delta K)^m$, coefficient m is $1 \times 10^{-7} \sim 3 \times 10^{-7}$ m/cycle.

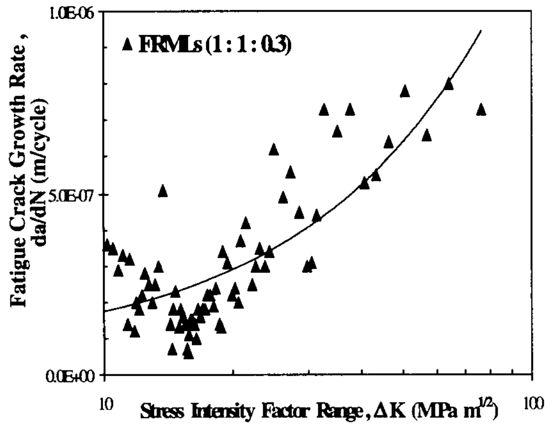
It is shown in Fig. 10 of the relation between the fatigue crack growth rate(da/dN) and the stress intensity factor range(Δ K). It shows that the crack of FRMLs(2) grows more slowly than FRMLs(1). The resin mixture ratio <1:1:0.2> shows the optimal fatigue failure properties because the slope is the lowest. However, the crack growth rate of resin mixture ratio <1:1:0.3> increases rapidly for over 30% accelerator content, and that is, the fatigue properties appears excessive accelerator content.



(a) Resin mixture ratio <1:1:0.1>



(b) Resin mixture ratio <1:1:0.2>



(c) Resin mixture ratio <1:1:0.3>

Fig. 10 Relation between fatigue crack growth rate (da/dN) and stress intensity factor range(⊿K) in FRMLs(2)

From the point of view of fatigue crack propagation rate(da/dN), the fatigue crack of FRMLs(1) propagates faster than that of FRMLs(2). It means that the addition of accelerator contributes to the improvement of the interlaminar bonding force.

In addition, FRMLs(1) of resin mixture ratios <1:0.5>, <1:0.75>, <1:1.5> and FRMLs(2) of resin mixture ratio <1:1:0.3> have similar data scatter. Considered that da/dN variation more accelerate than Δ K variation in except optimal resin mixture ratio with the resin mixture ratio <1:1> of FRMLs(1) and <1:1:0.2> of FRMLs(2). The relation between da/dN and Δ K shows that the slope is stiffer according to resin mixture ratio except optimal resin mixture ratio <1:1>, <1:1:0.2>. Coefficient m is shown approximately $1.5 \times 10^{-7} \sim 2.5 \times 10^{-7}$ m/cycle at FRMLs(1) and FRMLs(2).

4. Conclusion

In this study, the effect of the resin mixture ratio on mechanical properties and the fatigue crack propagation behavior of FRMLs(1) and FRMLs(2) was investigated. The obtained results are as follows.

(1) The bending strength of FRMLs(1) shows approximately 2 times more improved than that of Al 5052-H34 and the bending strength of FRMLs(2) shows approximately 2.2 times more improved than that of Al 5052-H34.

(2) In case of FRMLs(1), the resin mixture ratio <1:1> shows the maximum fatigue life, and in case of FRMLs(2), the resin mixture ratio <1:1:0.2> shows the maximum fatigue life. Accordingly, the optimal content of an accelerator is 20% of an epoxy resin content. On the whole, the fatigue life of FRMLs(2) increased to 16% longer than that of FRMLs(1).

(3) The fatigue crack propagation rate of FRMLs(1) and FRMLs(2) are longer than that of Al 5052-H34. Therefore the fatigue life of FRMLs(1) and FRMLs(2) was longer.

(4) The fatigue crack propagation rate(da/dN) of FRMLs(1) is higher than that of FRMLs(2).

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