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Development of the High Thermal Conduction Laminates for Large Current Board

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Abstract

With the objective of developing high thermal conductive laminates capable of being used as high current-carrying wiring boards for automotive and industrial applications, we identified the optimum blending method and optimum fillers for biphenyl-type epoxy resin that possesses high thermal conductivity, and studied laminating conditions. As a result, we established a method to achieve homogeneous dispersion and we manufactured prepregs that are devoid of coating irregularities. In addition, we found fillers capable of achieving a maximum thermal conductivity of 7.5 W/m·K and thereby enhanced both thermal conductivity and insulation resistance. Although copper-foil peel strength was reduced, we increased its strength by means of the roughening of rolled copper. In addition, we were able to determine molding conditions such as press temperature.

Foreword

In line with the fast-paced sophistication of electric and electronic equipment, laminates for making wiring boards have come to be used under increasingly hostile conditions. For example, wiring boards installed in the engine compartments of cars are exposed to high temperatures that sometimes exceed 100°C from heat generated by parts mounted on them and heat from components located in their surroundings. (See Figure 1) In the case of hybrid vehicles, for which demand has been growing as awareness of the environment increases, inverters are being used to power electric motors1). In step with the rising output power of drive motors, devising ways of dissipating the heat produced by switching devices that are responsible for controlling these drive motors while, at the same time, increasing the output power of the drive motors has become a challenge. (See Figure 2)

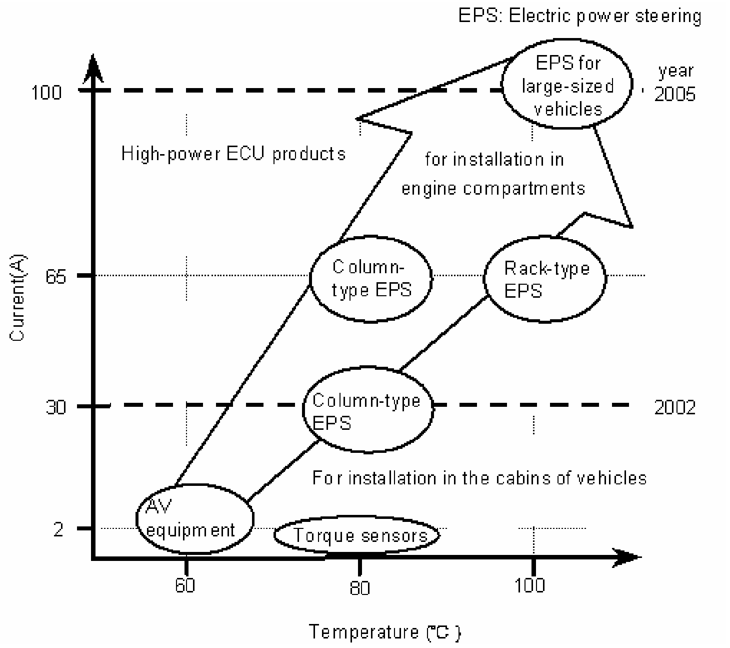


Figure 1 - Relationships between Current Used in ECUs and Temperature

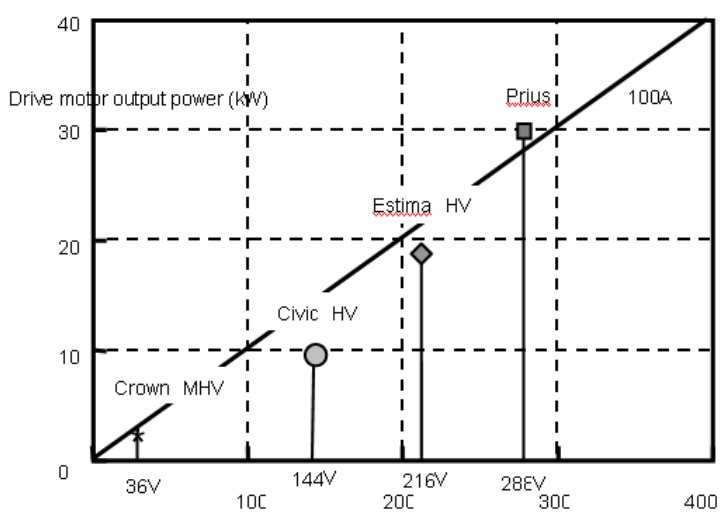


Figure 2 - Relationships between HV-Use Drive Motors and W/H Current[5]

Since these inverters must handle large currents and high voltages in particular, ceramic boards (substrates) having high thermal conductivity and excellent insulation properties are being used to mount devices. However, these ceramic boards have disadvantages such as being brittle, having relatively poor performance in withstanding voltage, and being very high in cost. Although attempts have been made to replace ceramic boards with resin boards, it is difficult to replace ceramic boards with resin boards that are incapable of effectively dissipating heat produced by devices; this is due to the fact that the thermal conductivity of conventional epoxy resin insulation layers is a mere 0.45 W/m·K (in the case of FR-4) as opposed to the thermal conductivity of insulated portions on ceramic boards, which measures 100 W/m·K or higher.

To enhance the thermal conductivity of laminates, it is necessary to use a resin material that has a high coefficient of thermal conductivity for manufacturing laminates. Composite materials produced by dispersing an inorganic filler such as alumina or silica in resin are generally used as high-thermal-conductivity resin materials. However, since the dispersion of an inorganic filler in resin significantly increases the viscosity of resin varnish, the workability and the ability to impregnate the base material with it make manufacture more difficult. Moreover, the flexibility of the hardened resin material decreases, resulting in deteriorated workability. It is, therefore, desired that inorganic fillers be used in as small amounts as possible. However, this runs counter to increasing thermal conductivity. To solve this problem, we decided to increase the thermal conductivity of resin itself.

Techniques to enhance the thermal conductivity of resin itself have already been studied at the Materials Research Laboratory, Hitachi, Ltd. based on the principles of thermal conductivity. Enhancement of thermal conductivity of resin itself is possible if high-order structures can be formed within resin, which are capable of controlling the scattering of phonons that serve as a thermal conduction medium. Figure 3 is a set of conceptual illustrations depicting this. Using monomers prepared by introducing structures called mesogens, which are rigid and lend themselves to orientation into molecules, macroscopically and isotropically positioning quasicrystalline higher-order structures in which the mesogens are microscopically and regularly aligned creates conditions conducive for heat to propagate in all directions. We increased thermal conductivity 1.7 times by using a biphenyl-type epoxy resin and causing it to form nematic liquid crystal structures. In addition, we achieved low thermal expansion, low water absorbency and high elasticity at high temperatures.

With an eye toward supplanting ceramic boards, we began development of high-heat-dissipation laminates with excellent heat-dissipation properties by employing a resin composite prepared by dispersing inorganic fillers into a biphenyl-type epoxy resin. We are conducting this development in teamwork with the Materials Research Laboratory, Hitachi, Ltd.

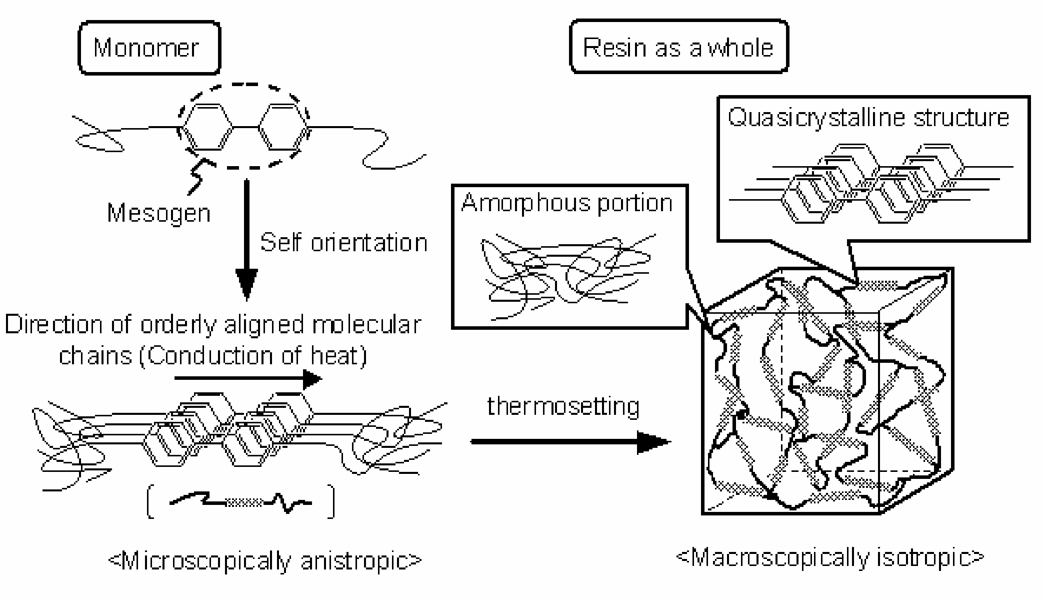
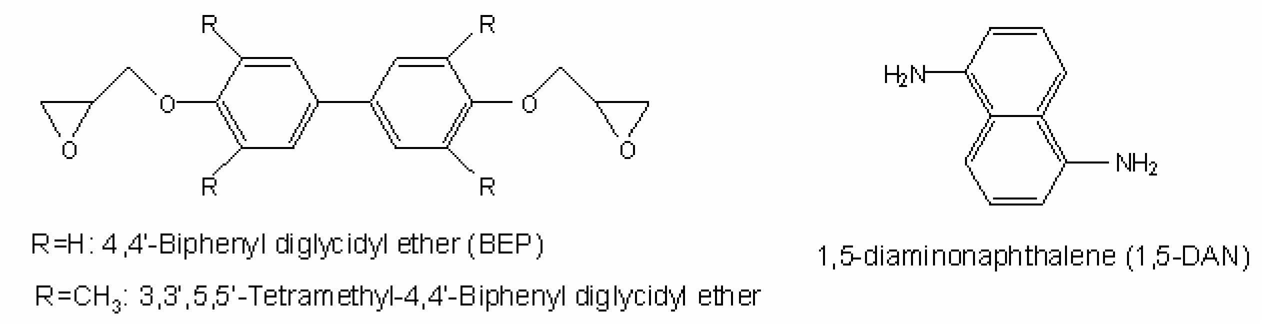


Figure 3 - Principles of High-Temperature Heat Conduction

Experimental

The resin and curing agent used are shown below. The YL6121H manufactured by Japan Epoxy Resins Co., Ltd. is an admixture of 4,4'-biphenyl diglycidyl ether (BEP) and 3,3', 5,5'-tetramethyl-4, 4'-biphenyl diglycidyl ether. On the other hand, 1,5-diaminonaphthalene (1,5-DAN), which is a diamine curing agent, is a product of the Nippon Steel Chemical Group. (See Figure 4) We manufactured laminates by means of the following method. Along with the biphenyl-type epoxy resin, the 1,5-DAN curing agent, and a filler such as magnesium oxide or boron nitride are added to active solvents such as methyl ethyl ketone (MEK). By blending this admixture, we obtained a varnish. We impregnated base materials such as glass fabric with this varnish, and then dried the varnish-soaked base materials in an oven, and thence obtained stage-B prepregs. We sandwiched one or more prepregs between two copper foils, and pressed this assembly using a vacuum press under a pressure of 4 MPa and under heat at a temperature of 175°C or 205°C for a duration of 90 minutes, and obtained a laminate. This manufacturing flow is shown in Figure 5. The obtained laminate was etched, cut or polished according to test purposes in order to make test pieces for characteristics evaluation purposes. Characteristics evaluations were made in accordance with such standards as JIS and IPC. We measured the coefficients of thermal conductivity of test pieces using a hot-wire method.



R=H: 4,4'-Biphenyl diglycidyl ether (BEP)

R=CH_3: 3,3',5,5'-Tetramethyl-4,4'-Biphenyl diglycidyl ether

1,5-diaminonaphthalene (1,5-DAN)

Figure 4 - Structure of Diepoxy Monomers and Diamine Curing Agent

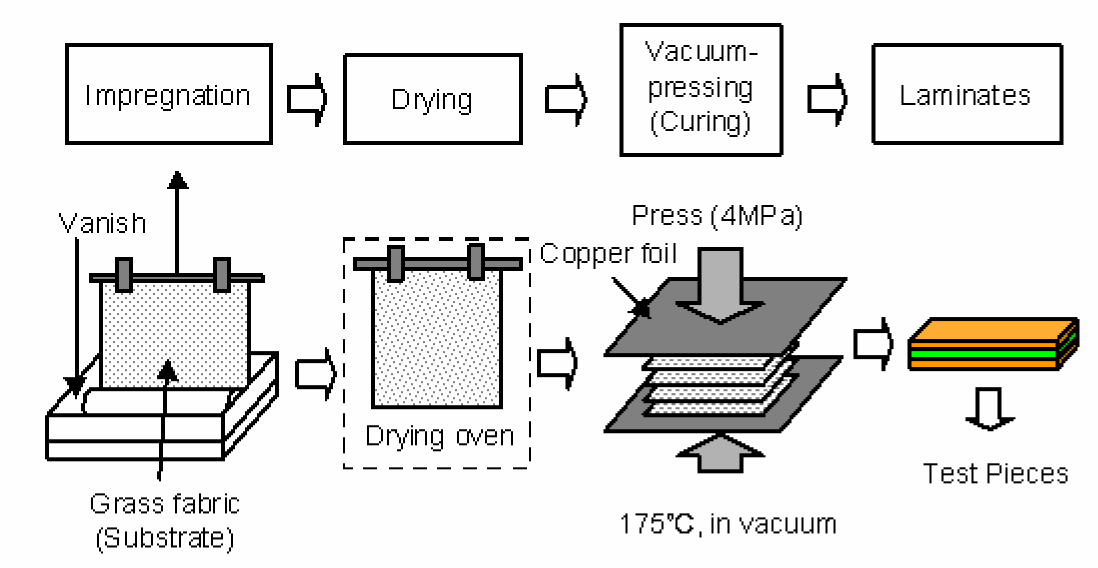


Figure 5 - Schematic Drawing of the Fabrication Process of Laminates

Results and Consideration

Study on a laboratory scale

As has already been explained in the experimental section, we prototyped laminates by impregnating a glass fabric base material with the varnish, and then pressing the varnish-soaked base material under heat and pressure. This time, we performed the prototyping on a laboratory scale merely for the purpose of determining whether the laminates would reach our target values. The solubility of the biphenyl-type epoxy resin we used this time was very low in the organic solvents, and low varnish viscosity resulted. As a result, sedimentation of the resin and filler occurred, and application inconsistencies developed. We have conducted measurements on these laminates in terms of the coefficient of thermal conductivity, coefficient of linear thermal expansion, adhesion strength, combustibility, and insulation resistance and have studied the feasibility of putting them to practical use as wiring boards.

The results of the measurements show that the coefficient of thermal conductivity of the laminates stood at a high 1.35 W/m·K, 2.5 times that of the current FR-4 (0.45 W/m·K). As for the coefficient of thermal expansion and copper-foil peel strength, the laminates scored equally well with the current product. Where flame retardancy is concerned, UL94V-0 was satisfied by the addition of an appropriate amount of a fire-retardant additive without degradation of thermal conductivity. (See Figure 6) However, since one of the fillers used this time was magnesium oxide, which absorbs humidity, insulation resistance deteriorated. (See Figure 7)

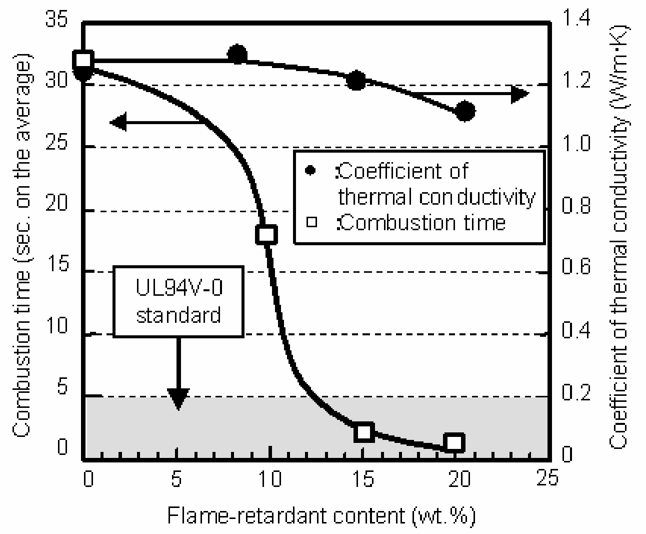


Figure 6 - Relationships between Br Content and Thermal Conductivity/Combustion Time

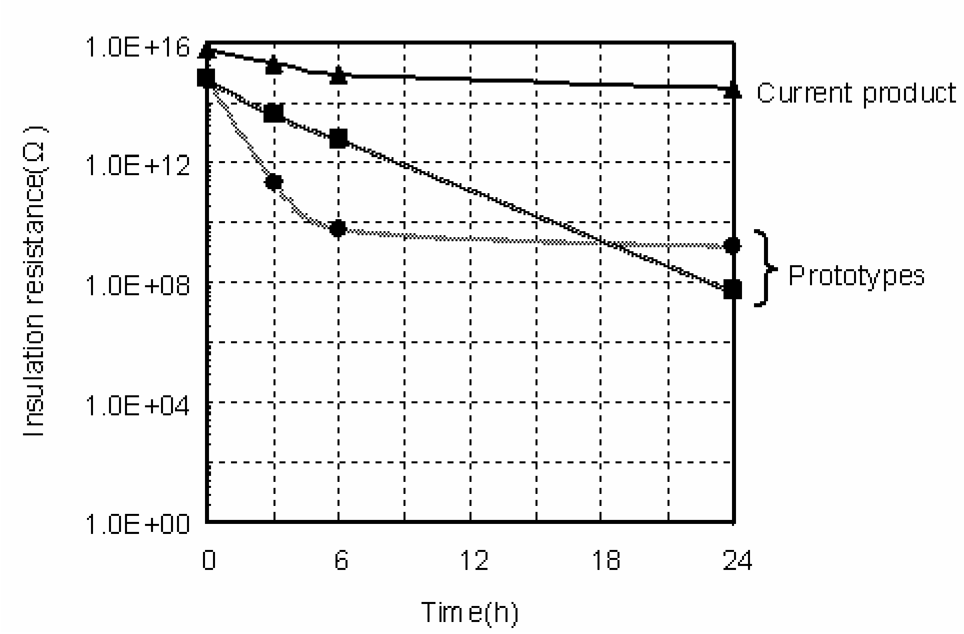


Figure 7 - Insulation Resistance Measurement Results

Present State of Highly Heat-dissipative Laminates and Their Problems

As has been discussed, our studies using the epoxy resin with mesogens serving as skeletal frames prove that our prototype laminates exhibit improved heat-dissipating performance. However, the laminates also have the disadvantages of moisture absorption-induced insulation-resistance deterioration and varnish dispersability. What is more, in order to meet the need for large-current-carrying boards, it is necessary to combine our prototype laminates, even though they are approximately 2.5 times higher in thermal conductivity than their current counterparts, with thick copper plates that have a high coefficient of thermal conductivity and a large heat capacity. However, when it comes to making copper plates exceeding 200 μm in thickness, a method other than the conventional electrolytic copper production method is required, and it is necessary for us to establish a molding method for their lack of roughened surface when manufacturing laminates. By factoring in the above-mentioned points, we conducted studies broadly under the following three themes in preparation for commercialization:

(1) Establishment of a method to homogeneously disperse resin and fillers
(2) Further improvement of thermal conductivity and enhancement of hygroscopic related insulation performance
(3) Studies on molding conditions with commercialization in mind

Establishment of a Method to Achieve Homogeneous Dispersion

Since the solubility of the biphenyl-type epoxy resin currently under study is very low in organic solvents, the viscosity of the varnish is also low, the sedimentation of the curing agent and fillers occurred, and application inconsistencies developed when the glass fabric base material was impregnated with the varnish. (See Figure 8) As explained, because it is difficult to completely dissolve the resin and curing agent, there is a need to homogeneously disperse all ingredients of the varnish, including the fillers. As one method to achieve homogeneous dispersion, we raised the viscosity of the varnish by the addition of a thickener. We have, therefore, tried a variety of thickeners. Although each thickener has its own viscosity-raising effect, none of them prevented the fillers from settling and none eliminated application inconsistencies. Next, we studied the possibility of achieving homogeneous dispersion in varnish by means of high-speed agitation with which to break particles loose more finely. We performed high-speed agitation experiments using a high-performance mixer and achieved homogeneous dispersion. As a result, the problem of filler sedimentation has been almost completely solved. (See Figure 9)

We performed varnish application using this varnish, and were able to obtain prepregs that were virtually free from application inconsistencies. On the strength of this result, we decided to conduct studies using varnish whose ingredients were homogeneously dispersed by means of high-speed agitation.

Figure 8 - Prepreg prepared without High-Speed Agitation

Figure 9 - Prepreg prepared with High-Speed Agitation

Further Improvement of Thermal Conductivity and Enhancement of Hygroscopic Related Insulation Performance

In our earlier studies, we used magnesium oxide possessing a thermal conductivity of approximately 30 W/m·K. With this, our prototype laminates indicated a coefficient of thermal conductivity (of 1.2 to 1.35 W/m·K), which was approximately 2.5 times higher than the current FR-4's thermal conductivity (of 0.45 W/m·K). However, in light of the fact that the thermal conductivity of insulated portions on ceramic boards exceeds 100 W/m·K, there is still plenty of room for improvement in terms of performance. Furthermore, we realized that one of the fillers we used was hygroscopic and gave rise to the problem of deteriorated insulation with moisture absorbed. We, therefore, conducted renewed studies on fillers and made improvements for increased thermal conductivity and insulation resistance.

This time, we used boron nitride (BN), which has a thermal conductivity of approximately 60 W/m·K and is non-hygroscopic by itself, as a filler. We used several varieties of BN that were surface-treated differently. We obtained homogeneous varnish dispersion by means of high-speed agitation using a high-performance mixer and prototyped laminates on a laboratory scale. The thermal conductivity of the laminates varied greatly from 3.2 to 7.5 W/m·K depending on the condition of their surface treatment and the amount of BN added. (See Figure 10) However, since, as has been discussed earlier, dispersing inorganic fillers in resin significantly raises the viscosity of resin varnish, there is a limit to the amount of such fillers that can be added.

Figure 11 shows the hygroscopicity of prototyped laminates. When the prototyped laminates were treated for up to 24 hours in a pressure cooker at 121°C, 2 atmospheres, 100%RH, no interlaminar separation took place unlike in our last experiment. In addition, we found that the prototyped laminates were equal to or better than the current FR-4 in terms of insulation resistance value. Thus, the use of BN has enabled us to find a filler that attains both enhanced thermal conductivity and insulation resistance characteristics.

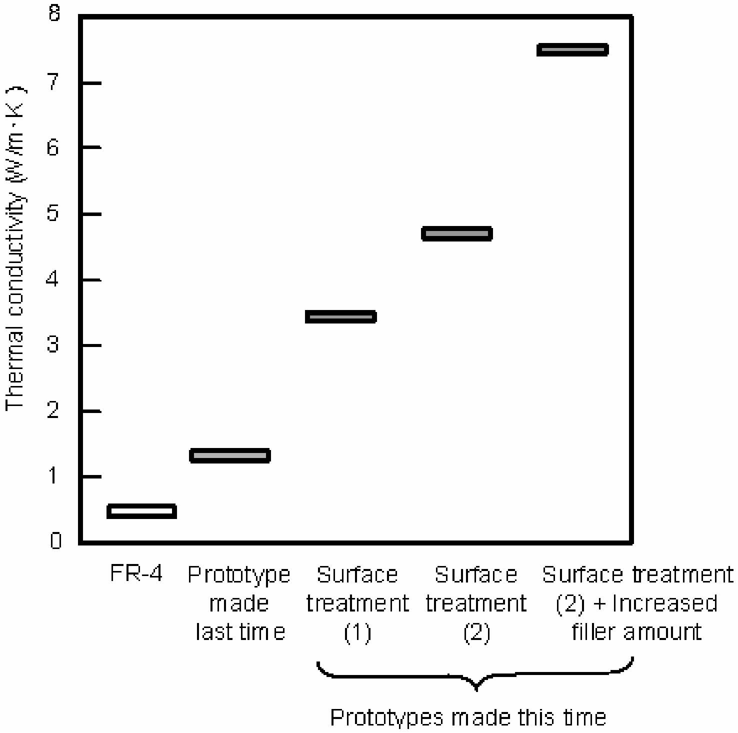


Figure 10 - Thermal Conductivity Measurement Results

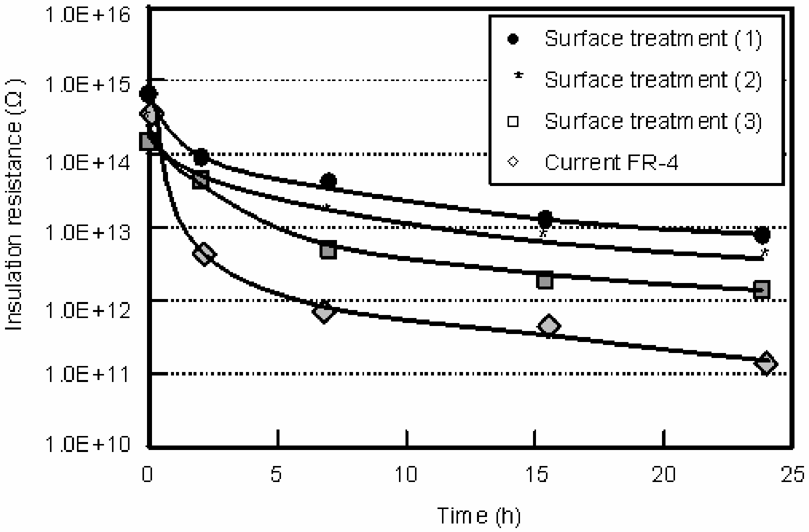


Figure 11 - Pressure-Cooker Treatment Time (h)

Studies on Molding Conditions with Commercialization in Mind

Through the studies we conducted, we have been able to obtain higher coefficients of thermal conductivity and insulation resistance values that were equal to or better than the current FR-4. However, since they represent the results of our studies conducted on a laboratory scale, it is necessary for us to decide upon optimum base materials, molding conditions and the like. What is more, when laminates are to be used as large-current-carrying wiring boards, the use of thick copper plates is unavoidable for creating onboard circuit traces. This necessitates a study of molding conditions for a combination of rolled copper and highly heat-dissipative laminates. With this being the situation, we conducted studies on lamination conditions and base-material selections. As for the varnish selection, we used a varnish that we had previously studied. As for the filler selection, we employed the filler that measured a thermal conductivity of approximately 5 W/m·K shown in Figure 10 in light of a combination of workability and various characteristics. In our subsequent highly-heat-dissipative-varnish-applied studies, we used the same filler and the same varnish with the same constituent proportions. We performed varnish application using vertical applicator equipment intended for prototyping applications. As for copper, we used 300-μm-thick rolled-copper plates that had undergone roughening treatment and a molding process under heat and pressure exerted by a vacuum press.

The results of various studies we conducted are described in the section that follows.

Studies on Base Materials

For use as base materials, candidate materials include glass fabric, nonwoven glass fabric, nonwoven aramid fabric as well as more exotic materials such as alumina fiber, carbon fiber and other organic fibers.

For use as laminated wiring board substrates, we prototyped laminates using glass fabric, nonwoven glass fabric, and nonwoven aramid fabric, all of which are commonly used base materials. The results of our measurements conducted for a variety of characteristics are shown in Table 1. Although the nonwoven glass fabric displayed a high thermal expansion coefficient, its other characteristics did not excessively degrade. In addition, the glass fabric and nonwoven aramid fabric produced more of the same results. These results indicate that we can change base materials in accordance with the required characteristics such as board thickness.

Table 1 - Various Measurement Results

Measurement item	Current heat-resistant material	Glass fabric	Non woven glass fabric	Non Woven aramid fabric
Thermal conductivity (W/m·K)	0.5	5.1	5.1	5.8
Thermal Expansion coefficient (ppm/K)	15.5	15.3	28.3	13.8
Combustion testing (sec)	UL94 V-0	UL94 V-0	UL94 V-0	UL94 V-0
Copper foil peel strength (kN/m)	1.0	0.27	0.24	0.26
Insulation resistance (Ω) (after 24-hr-long treatment in pressure cooker)	9.2E+10	9.8E+11	5.8E+11	8.3E+12
Achievable base material thickness (μm)	80 ~ 200	80 ~ 200	100 ~ 600	50 ~ 100

As one characteristic-related finding, we found that the peel strength of the copper foil was extremely low. Observations of cross sections under an electron microscope revealed that destruction occurred at interfaces between the filler and the resin and, thereby, degradation of adhesion strength between them resulted. To solve this problem, we improved peel strength by making chemical and physical modifications to the filler. In some cases, furnishing SiO_2 treatment to the filler or blending two or more kinds of fillers resulted in increased copper-foil peel strength. However, since the thermal conductivity decreased in such instances, we concluded that it is difficult to enhance copper-foil peel strength through chemical and physical treatment.

On the other hand, the roughening of copper foil produced an only small improvement in copper-foil peel strength, but without incurring a penalty in thermal conductivity. Based on this finding, we decided to improve the copper-foil peel strength by means of increases in surface area and thereby enhanced anchoring effects by adjusting the amount of roughening of the copper foil.

Study of Roughening Conditions

In the case of electrolytic copper foil used as a commonplace electronic material, roughened surfaces are electrochemically produced as a result of its manufacturing process. On the other hand, rolled copper foil has no roughened surface, and it is necessary to subject it to surface-roughening treatment in advance of the molding of copper-foil-sandwiched laminates. Conventionally, blackening treatment was used. However, this treatment gives rise to the problem of degradation of adhesion when undergoing thermal treatment, and it does not lead to the improvement of copper-foil peel strength. For this reason, this time, we tried to increase copper-foil peel strength by employing a roughening treatment called microetching and studying the relationships among roughening time, the amount of roughening, and copper-foil peel strength. The results of this trial are described below.

Firstly, we determined the relationship between the amount of microetching-caused roughening and copper-foil peel strength by using current prepregs featuring high copper-foil peel strength. (See Figure 12) As a result, it was found that the greater the amount of roughening, the higher the copper-foil peel strength and the post-heat-treatment-retention rate. Since the result of comparisons with current prepregs using electrolytic copper foil has confirmed that the minimum required amount of roughening stood at 7.5 μm, we have decided to adopt this roughening amount for our subsequent studies.

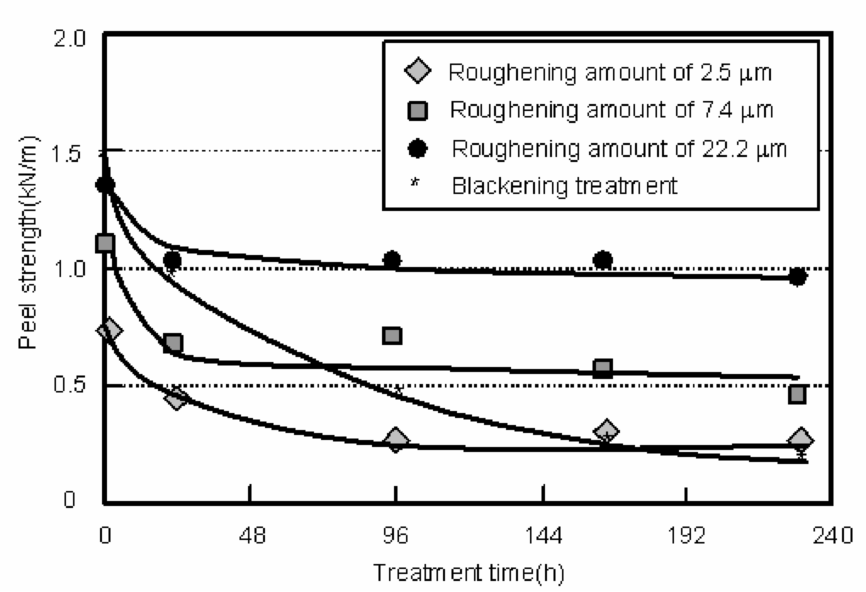


Figure 12 - Relationship between the Amounts of Roughening and Peel Strength

Next, we fabricated laminates using the highly heat-dissipative prepregs that exhibited low copper-foil peel strength, and measured their copper-foil peel strength. The result of the measurement showed some gain in copper-foil peel strength, reaching approximately 0.6 kN/m, but fell short of our target value of 1.0 kN/m. We, therefore, additionally performed blackening treatment subsequent to the microetching treatment. Measurement indicated that copper-foil peel strength measurement increased to approximately 0.8 kN/m. As this value still falls short of the target value, further studies are required.

Studies on Press Temperature Conditions

Of laminate conditions, one factor that significantly influences product characteristics is press temperature. Table 2 shows the results of measurements of various characteristics conducted at a current press temperature of 175°C and a newly raised press temperature of 205°C.

Although both measurement results under the headings "Coefficient of thermal conductivity" and "Copper-foil peel strength" remained more of the same, there was a rise of 10°C to 20°C and an increase of 1,000 MPa under the headings "Tg" and "Storage modulus," respectively. Since a high Tg is the most important factor on the path toward commercialization, we decided upon 205°C as a press condition.

Table 2 - Various Measurement Results

Press temperature	175°C	205°C
Base material used	Non woven aramid fabric	Non woven aramid fabric
Coefficient of thermal conductivity (W/m·K)	4.9	5.2
Coefficient of thermal expansion (ppm/K)	15.5	15.7
Copper-foil peel strength (kN/m)	0.23	0.25
Tg (°C) (DMA method)	172	192
Storage modulus (MPa) (DMA method)	2130	3425

Conclusion

We conducted studies on laminates using highly-heat-dissipative varnish and reached the following conclusions.

We found fillers that give rise to high thermal conductivity and high insulation resistance when they are blended with biphenyl-type epoxy resin and established a homogeneous dispersion method that makes it possible for us to make prepregs that are free from application inconsistencies. Furthermore, we optimized molding conditions such as press temperature and gained increases in copper-foil peel strength by subjecting rolled copper foil to roughening treatment. However, further enhancement of copper-foil peel strength and more detailed formulation of press conditions remain challenges to be addressed. After overcoming these challenges, we will proceed toward commercialization.

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