

DISMANTLABLE EPOXY ADHESIVES FOR RECYCLING OF STRUCTURAL MATERIALS

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Abstract

A novel adhesive, consisting of well-formulated epoxy resins and thermally expansive fillers has been developed. The cured adhesive resin showed characteristic viscoelasticity with both the storage modulus higher than 3 GPa in the glassy state under the glass transition temperature (T_g) around 100 °C and the rubbery modulus less than 2 MPa over the T_g . As the results, the joint bonded with the adhesive was strong at ambient temperature under 80 °C and they could be dismantled easily at high temperature due to the expansion force caused by expandable graphite as the fillers. The technique of the dismantlable adhesive joints should be important in terms of material recycling because carbon fiber reinforced plastics (CFRP) has to be separated in the recycling process from the other materials such as steel or aluminum alloy used as parts of automobiles, for example.

1 Introduction

Recently, material recycling of industrial products is important from the viewpoint of the environmental issue. For recycling, dismantlement is necessary for separating several materials used in a product and reusing them. In automotive industries, the use of CFRP is increasing. If the parts of CFRP are bonded adhesively to the other parts consisting of metals such as aluminum alloys, the importance of recycling is enhanced much more, because CFRP is relatively high cost materials. Therefore, a novel technology, which easily dismantles the adherents, is required.

One of authors has researched a dismantlable adhesive including thermally expansive microcapsules [1]. The thermally expansive microcapsule consists of plastic shells filled with liquid hydrocarbon. The microcapsule can expand at high temperature. This mechanism enabled to

peel off the adherents easily using heat energy, as illustrated in Fig.1. [2].

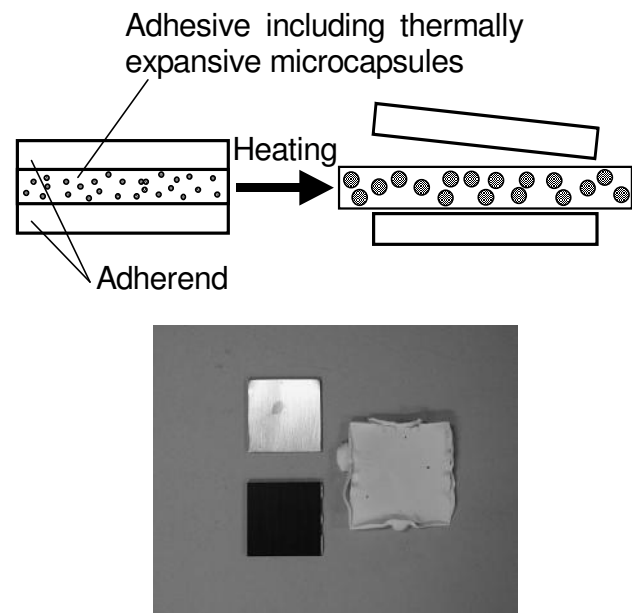


Fig.1. A schematic illustration of a dismantlable joint and a dismantle test result of the joint between CFRP and Aluminum plates [2]

Though the adhesive showed an intermediate strength of 13 MPa, the high temperature performance was poor because the microcapsules began to expand around 60 °C and the T_g of the adhesive resin was lower than the expand temperature of microcapsules. For structural applications such as automobiles, high temperature performance is essential.

Therefore, new dismantlable adhesive with high adhesive performance even at high temperature is required. In US-JAPAN conference on composite materials in 2006, we presented a paper mainly focused on expandable graphite as the other expansive fillers with higher temperatures to begin

expansion such as 150 °C, 200 °C or much higher. This paper firstly presents the designing philosophy of matrix resin formulation for the dismantlable adhesives including the expandable graphite [3]. Secondly, the adhesive properties, the dismantlable performance, and their mechanisms are discussed.

2 Experimental

2.1 Materials

2.1.1 Epoxy resins and curing agents

Two types of di-functional epoxy resin DGEBA (Diglycidyl ether of bisphenol-A) were used as main components for adhesive resins. One was Ep828 with 189 g /eq. of epoxy equivalent and another was Ep1001 with 475 g / eq. of epoxy equivalent. Three kinds of mono-functional epoxy monomers: GPI (N-glycidyl phtalimide), TBPGE (p-tertiary butyl phenylglycidyl ether) and EOG (phenol polyethylene oxide glycidyl ether) were compared as modifiers. GPI has higher polarity than TBPGE, EOG, and DGEBA.

As curing agents, 2MZ (2-methyl imidazole) or a mixture of DICY (Dicyandiamide) and DCMU (3-(3, 4-dichloro phenyl)-1,1-dimethyl urea) were used. The molecular structures of the epoxy resins and the curing agents are shown in Fig.2.

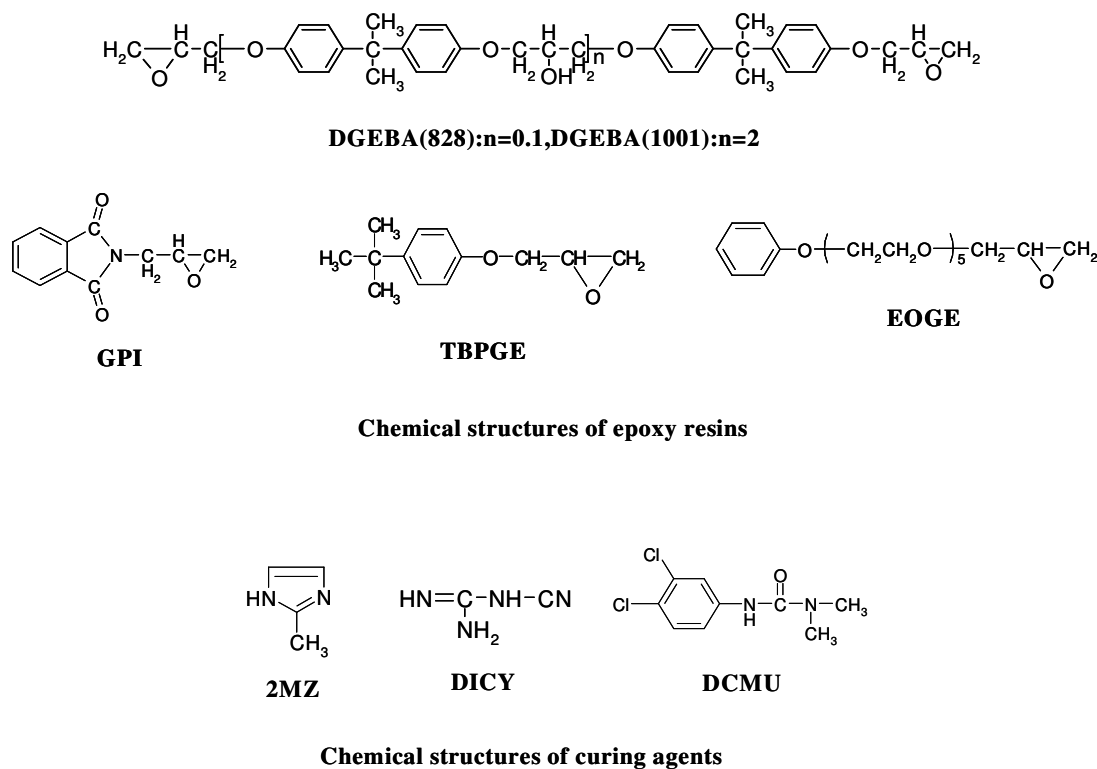


Fig.2. Chemical structures of epoxy resins and curing agents

2.1.3 Toughening modifiers

Pre-formed core-shell rubber particles EXL2655 manufactured by Kureha Industries, Inc, Japan were utilized as toughening modifiers. They were constituted of polybutadiene as the core and poly (methyl methacrylate) as the shell. The particle size was in the range from 0.1 to 0.6 μ m.

2.2 Evaluation methods

2.2.1 Preparation of cured resins

In order to prepare modified resin specimens, the epoxy mixture was first heated to 120 °C to lower the viscosity of the resin. In case of using toughening modifiers, the pre-formed particles were added slowly into the resin mixture and blended in first by hand and then mechanically stirred for 1hr. After adding curing agents at 60°C, the resin compositions were held at 80 °C under a vacuum to de-gas. The resin compositions were poured into preheated silicone-coated molds and cured at 120 °C for 1 hour.

2.2.2 Viscoelastic properties of cured resins

Temperature dependencies of the viscoelastic properties (storage modulus: E') of the cured bulk resins were evaluated by dynamic mechanical analysis (DMA) method in the bending mode using a dynamic frequency of 1 Hz. Samples were tested over a temperature range between 25 °C and 200 °C with a heating rate of 2 °C /minute.

2.2.3 Fracture toughness of the cured resins

Fracture toughness (K_{IC}) measurements on bulk resins were conducted using pre-cracked specimens with single edge notched 3-point bending configuration in accordance with ASTM D 5045-91.

2.2.4 Shear adhesive strength

Test specimens were prepared using aluminum substrates that had been wiped with acetone to prepare the surfaces for bonding. The dimensions of the aluminum substrates were length 150 mm, width 25 mm, and thickness 1.5 mm. Adhesive resin was applied to an aluminum substrate and then brought into contact to the other substrate, and the bonded joint was cured at 120 °C for 1 hour. The adhered lap length was 10 mm. The tensile shear adhesive strength of the specimens was evaluated using the test machine “INSTRON 5582” in accordance with JIS K 6850 at a crosshead speed of 10 mm/min at 23 °C, or 80 °C for high temperature tests.

2.2.5 Peel adhesive strength

The dimensions of the aluminum substrates were length 200mm, width 25mm, and thickness 0.5mm. Adhesive resin was applied to both aluminum substrates and then brought into contact, and the bonded joint was cured at 120 °C for 1 hour. The T-peel adhesive strength of the specimens with / without the toughening modifiers was evaluated using a test machine “INSTRON 5582” in accordance with JIS K 6854-3 at a crosshead speed of 100 mm/min at 25 °C.

2.2.6 Dismantlability

In order to examine the dismantlability of formulated adhesives, the specimens or parts jointed by the adhesive resins were exposed at 250 °C for 5 minutes in an oven. Then, the residual shear strengths of the joints after the heat treatment were evaluated. If the strength is zero, it means that the joint can be dismantled autonomously by the heat treatment.

2.2.7 Scanning electron microscopy observation

Fractured surfaces of the cured bulk resins after fracture toughness tests and fractured surfaces from adhesive tests were observed using a scanning electron microscope (SEM) “KEYENCE VE-8800”. The samples were mounted on brass stubs and were coated with a thin layer of gold using an ion sputter coater “JFC- 1100E” made by JEOL, Japan.

3 Designing philosophy of resin formulation for dismantlable structural adhesives

The formulation of matrix resin with the expandable graphite is important to improve the heat resistance of the dismantlable adhesive. Existing heat-resistant structural adhesives have high T_g , high modulus and high strength in the service temperature. They, however, also have relatively high modulus even in the rubbery state over T_g . The nature deteriorates the heat-dismantlability of the adhesives even including expansive fillers, because the hard resin is difficult to be expanded by the expansive fillers. On the other hand, the existing dismantlable adhesives have poor high temperature performance due to the low T_g . The idealistic property of resins for structural dismantlable adhesives is to possess both high T_g and low modulus and strength in the rubbery state over T_g [3]. In order to realize this, the development of new resin formulation with steep decrease of modulus

over T_g region is required, as shown in Fig. 4. Also, the expansive pressure of fillers should be high enough to surpass the modulus of resin in the rubbery state.

The scope of this research is proper formulation of the chemical composition of the resins to achieve both heat resistance and dismantlability together. For the purpose, not only the usual di-functional epoxy resin, but also mono-functional epoxy monomers were applied, and finally a well-formulated epoxy resin with thermally expansive fillers has been developed.

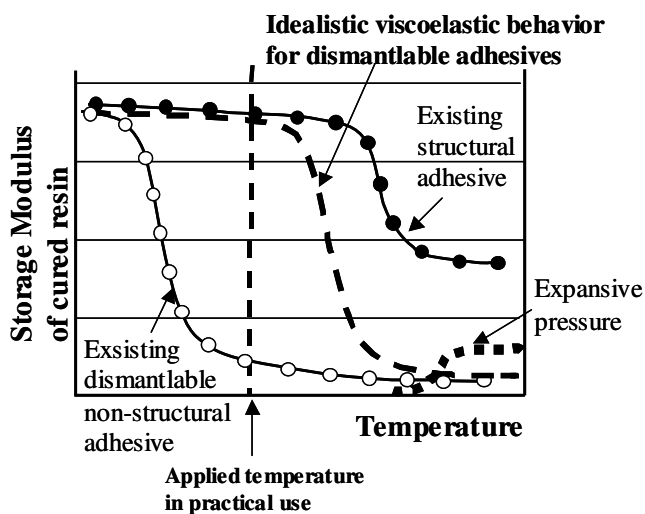


Fig.4. An idealistic viscoelastic behaviour of a cured resin for dismantlable structural adhesives.

4 Results and Discussion

Fig.5. shows the storage moduli of the 2MZ-cured resins consisting of DGEBA formulated with GPI, TBPGE or EOG. Although the T_g of the resins including the mono-functional epoxy monomers were lower than the pure DGEBA, the cured resin formulation with GPI as the mono-functional epoxy indicated higher T_g than the resin with TBPGE and the resin with EOG. The relatively high T_g of the resin with GPI would be caused by the high polarity and the rigidity of the imide-ring structure in GPI. In addition, since the modulus in the rubbery state of the resin with GPI was lower than the pure DGEBA, the heat-dismantlability of the resin formulation can be expected. Namely, GPI was most appropriate within the mono-functional epoxy monomers.

Curing agents also had an important role on the heat softening behavior, as shown in Fig.6. The combination of DICY / DCMU as the curing agents showed good balance on high T_g and steep softening

over T_g. Fig.7 shows the effect of GPI content in epoxy formulations on the storage moduli of DICY / DCMU cured resins.

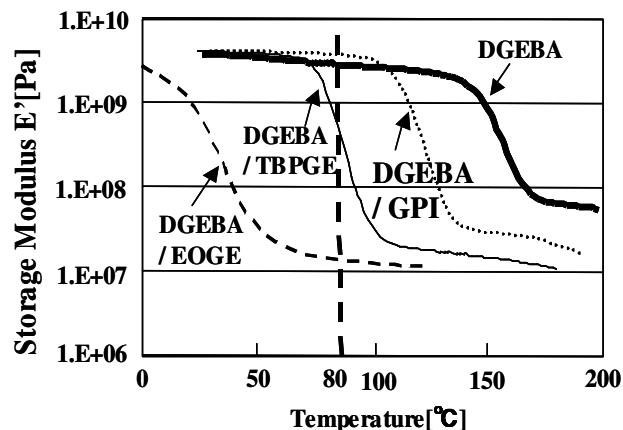


Fig.5. Temperature dependence of storage moduli of cured resins (DGEBA, DGEBA:GPI=60:40, DGEBA:TBPGE=60:40, DGEBA:EOGE=60:40, All resins were cured by 2MZ).

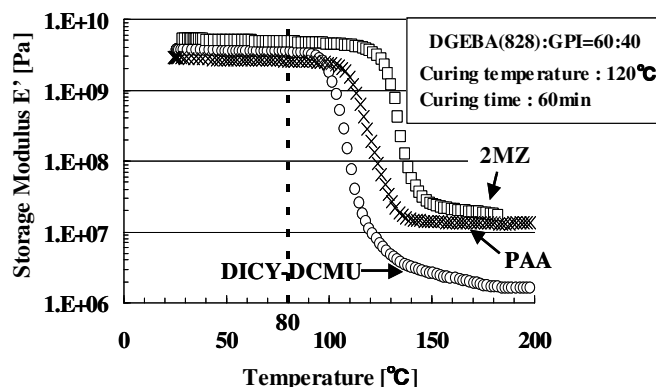


Fig.6. Effect of curing agent on temperature dependence of storage moduli of cured epoxy resins with an epoxy formulation. PAA: Polyamideamine.

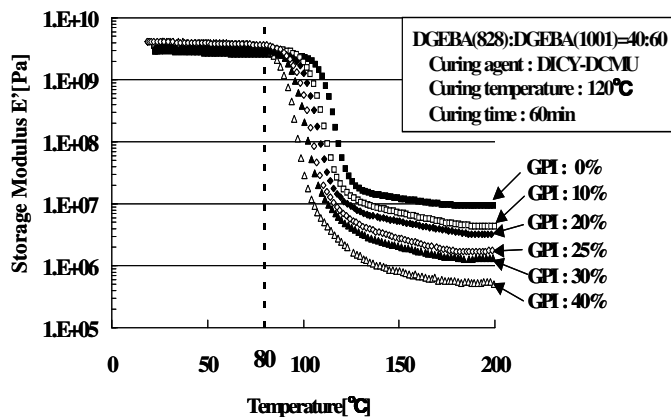


Fig.7. Effect of GPI content in epoxy formulation on storage moduli of cured epoxy resins

Peel strength and shear strength of adhesive joints using the resin formulations cured by DICY / DCMU were evaluated, as shown in Fig.8.

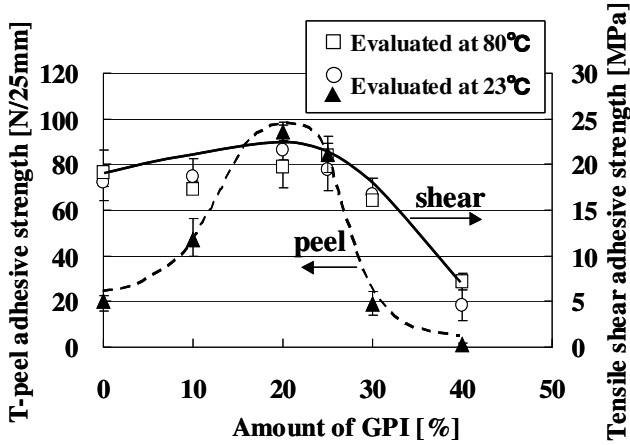
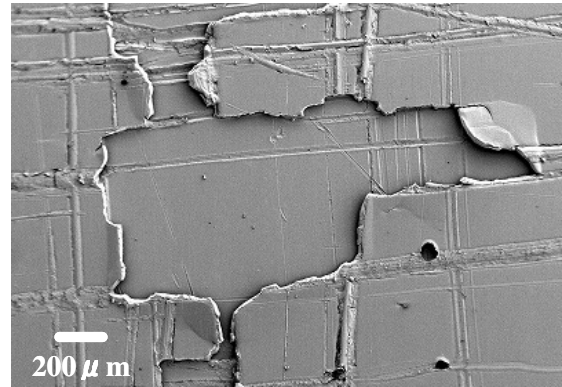


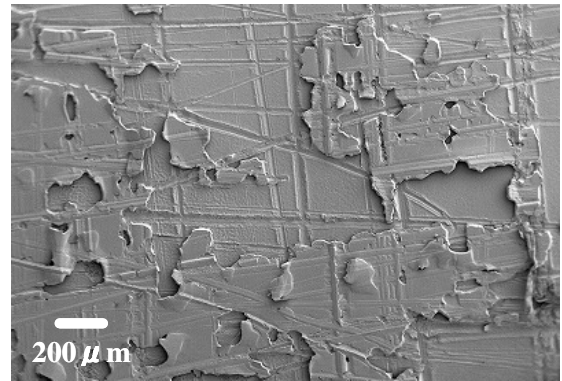
Fig.8. Effect of GPI content in epoxy formulation (DGEBA(828)/DGEBA(1001) = 40 / 60) on adhesive properties. Adherents: aluminum plates.

Both peel and shear adhesive properties depended on the GPI content in the formulation of epoxy resins. Especially, GPI content had a strong effect on the peel adhesive property. About 20 – 25 wt% addition of GPI made maximum peel strength. Fig.9 indicates the observed fracture surfaces by SEM in the specimens of peel adhesive tests. The fracture mode changed from interface-failure type to cohesive-failure type with increasing the GPI content. The effect of GPI addition on increasing interface affinity between epoxy resins and aluminum has been reported [4]. The addition of GPI also gave strong influence on the fracture toughness of the bulk resins. Fig.10 shows the relationship between GPI content and the fracture toughness (K_{IC}) of the bulk resins made of the adhesives. From zero to 20 wt% of GPI addition had a positive effect on the K_{IC} of the bulk resins, but more GPI addition over 20 wt% indicated a negative effect on the K_{IC} . It is reasonable that the adhesive properties would be under the influence of the mechanical properties of the bulk resins, especially in the case that the fracture modes of adhesive tests are cohesive-failure type. The measured peel adhesive properties of the resins showed exactly similar trend to the fracture toughness of the bulk resins in terms of the effect of GPI content. With increasing the fracture toughness of the resins, the peel-adhesive strength increased.

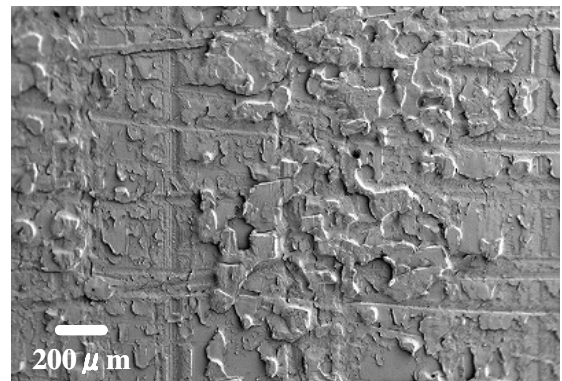
With decreasing the fracture toughness, the peel-adhesive strength decreased.



(a) GPI : 0%



(b) GPI : 10%



(b) GPI : 25%

Fig.9. Fracture surfaces observed by SEM after peel adhesive tests, in relation to GPI content in epoxy formulation. Adherents: aluminum plates.

- (a) DGEBA(828)/DGEBA(1001) = 40 / 60
- (b) DGEBA(828)/DGEBA(1001)/GPI = 36 / 54 / 10
- (c) DGEBA(828)/DGEBA(1001)/GPI = 30 / 45 / 25

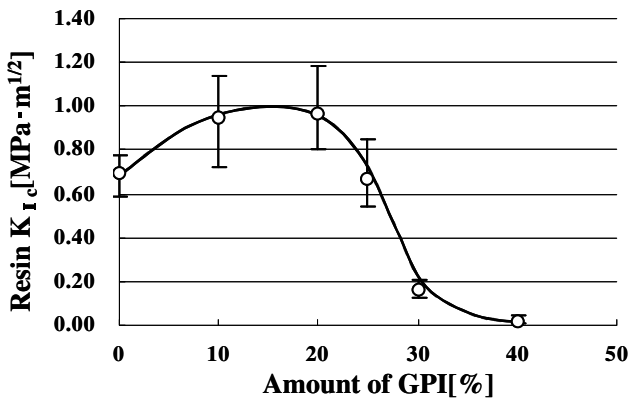


Fig.10. Effect of GPI content in epoxy formulation (DGEBA(828)/DGEBA(1001) = 40 / 60) on fracture toughness of cured bulk epoxy resins

These findings led to the base resin formulation with 25% of GPI. The cured base resin indicated the T_g around 100°C, storage modulus over 3GPa at glass state, and rubbery modulus lower than 2MPa, as shown in Fig.7. Then, the combination of the base resin formulation with 25% of GPI and 10% of expandable graphite fillers enabled good dismantlability. Residual strength of the joints after heat treatment of 250 °C for 5 minutes was zero. This means that the joint can be dismantled autonomously by the heat treatment. The lap shear strength of the joint without heat treatment for dismantlement was 15 MPa at R.T. or higher than 20 MPa at 80 °C, as shown in Figure 11.

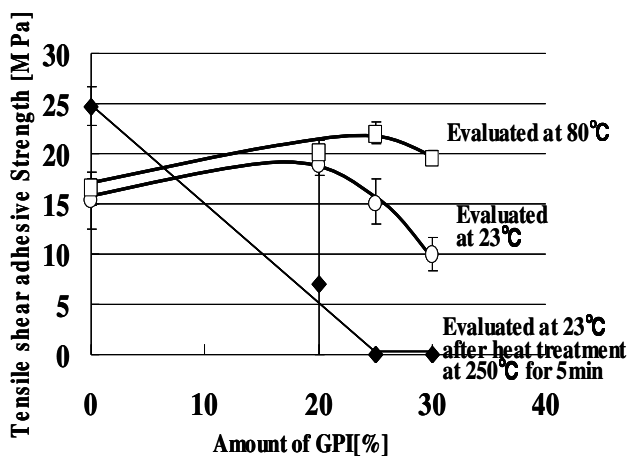


Fig.11. Influence of GPI content in epoxy formulation (DGEBA(828)/DGEBA(1001) = 40 / 60) with 10 wt% of expandable graphite on shear adhesive properties and dismantlability.

However, the peel adhesive properties of the resin decreased with including expandable graphite fillers. Without the expandable graphite fillers, the peel adhesive strength of the base resin formulation with 25% of GPI was 85N / 25mm at R.T. On the other hand, the resin with 25% of GPI and 10% of expandable graphite was 45N / 25mm at R.T., which was not enough for structural application.

Therefore, toughening of the adhesive resin was explored. Pre-formed core-shell rubber (CSR) particles, EXL2655, were blended as toughening modifiers into the base resin formulation with 25% of GPI. The fracture toughness of the modified resins was shown in Fig.12 in relation to the amount of CSR. With increasing the amount of CSR, the fracture toughness of the resins increased.

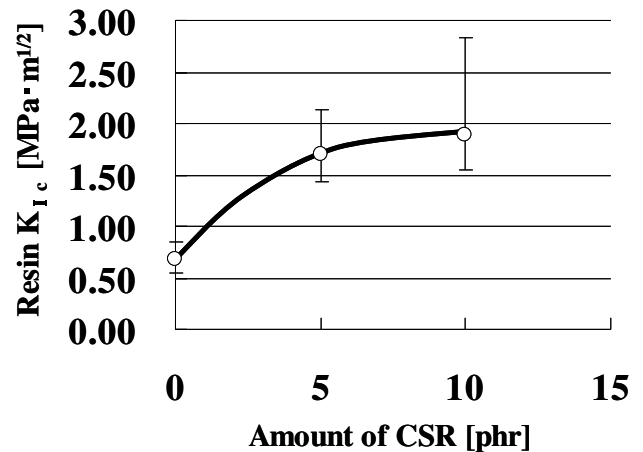


Fig.12 Effect of CSR content on fracture toughness of cured epoxy resins. The base epoxy formulation: DGEBA(828)/DGEBA(1001)/GPI = 30 / 45 / 25.

The storage modulus of the cured resin decreased slightly with increasing the amount of CSR in the glass region, as shown in Fig.13. However, the T_g was kept in almost same temperature as the base resin without CSR. Therefore, CSR was recognized as a candidate modifier for toughening the adhesive resins.

Peel adhesive properties of the modified resins were shown in Fig.14 in relation to the amount of CSR. Although addition of expandable graphite itself had negative influence to peel adhesive strength, the peel adhesive strength increased with increasing the amount of CSR, in both cases with and without expandable graphite. Even the case with 10 wt% of expandable graphite, the peel

adhesive strength reached 100 N / 25 mm by 10 phr of CSR, which was enough to apply in structural applications.

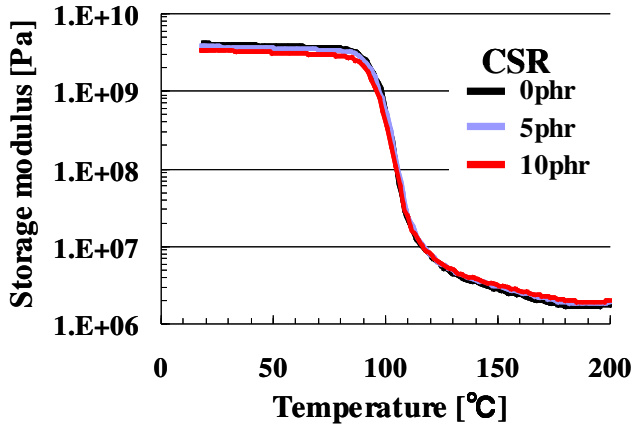


Fig.13 Effect of CSR content on storage moduli of cured epoxy resins. The base epoxy formulation: DGEBA(828)/DGEBA(1001)/GPI = 30 / 45 / 25.

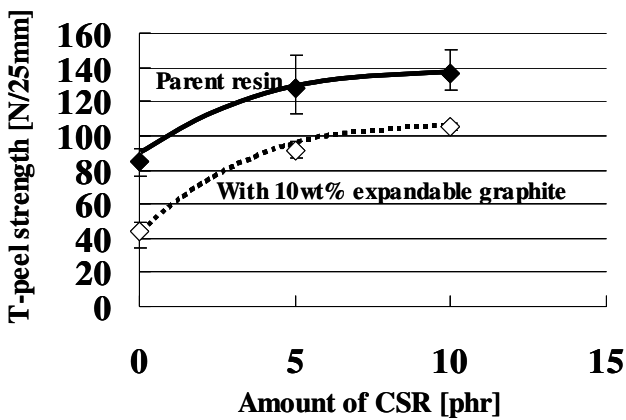


Fig.14 Effect of CSR content on T-Peel adhesive strength of epoxy resins. The base epoxy formulation: DGEBA(828)/DGEBA(1001)/GPI = 30 / 45 / 25 / 45 / 25.

Fig.15 showed the fracture surface observed by SEM after the peel adhesive tests. The epoxy formulation was DGEBA(828)/DGEBA(1001)/GPI = 30 / 45 / 25 with 10 phr CSR, without expandable graphite. The observation shows that the rubber toughening mechanism includes cavitation of the rubber particles and localized yielding of the epoxy matrix around the cavitated particles. The shear

yielding and the observed large amount of plastic shear deformation of the epoxy matrix would be responsible for absorbing the external energy. Yee and co-workers [5-8] have elucidated the toughening mechanisms in the elastomer-toughening technique. According to these authors, the role of the elastomer particles is to relieve the constraint in front of the crack tip by cavitation [6, 7]. This mechanism alters the stress field from one dominated by triaxial stress, which causes brittle fracture, to one dominated by shear stress, which promotes the formation of shear bands in the matrix resin [5-7]. Following this context, the change in the stress state by cavitation of rubber particles is considered to be a trigger for the formation of shear deformation of matrix. Additionally, the vital requirement for the toughening to be effective is intrinsic ability for plastic deformation of the matrix resin itself. In general, low cross-linked epoxy network can be deformed easier than highly cross-linked one [8]. In this research, we modified the matrix to be low cross-linked nature for achieving heat-dismantlability. This action would also help to achieve the rubber-toughening and the increased high peel adhesive properties.

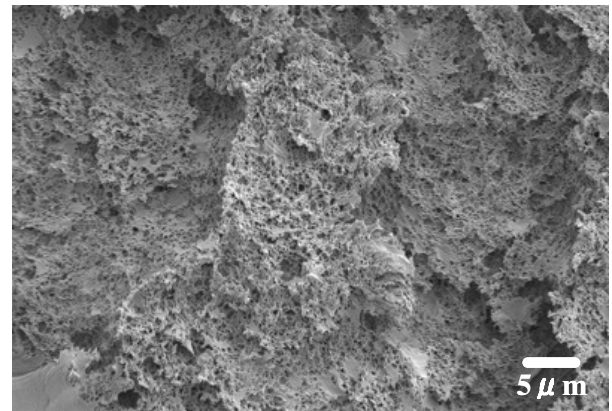
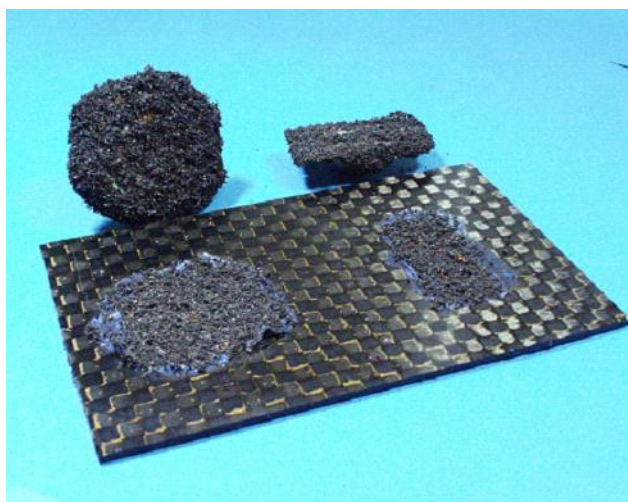


Fig.15. Fracture surface observed by SEM after peel adhesive test. The epoxy formulation is: DGEBA(828)/DGEBA(1001)/GPI = 30 / 45 / 25 with 10 phr of CSR. Adherents: aluminum plates.

Lastly, from practical viewpoints, dismantle tests were conducted using joints consisted of a CFRP and steel plates adhered with the dismantlable adhesives: DGEBA(828)/DGEBA(1001)/GPI = 30 / 45 / 25 with 10 phr CSR and 10 wt% of expandable graphite. After 5 min exposure at 250 °C, the parts were completely dismantled as expected, shown in Fig.16.



(a) Joints consisted of a CFRP and steel plates adhered with dismantlable adhesives (DGEBA (828) / DGEBA (1001) / GPI = 30 / 45 / 25 with 10 phr of CSR and 10 wt% of expandable graphite)



(b) Dismantled joints after heating at 250 °C for 5 minutes

Fig.16. A dismantle test results of the joint between CFRP and steel plates.

5 Conclusions

To realize the heat resistant dismantlable structural adhesive, the modification of resin was carried out and a promising resin composition has been developed. The resin consists of DGEBA, GPI as epoxy monomers, DICY / DCMU as curing agents, including expandable graphite (80LTE-U) as expansion fillers. The adhesive had both shear

adhesive strength higher than 20MPa at 80 °C and a good dismantlability at 250 °C. The peel adhesive strength was improved by addition of CSR particles without deteriorating the dismantlability.

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