

# Adhesive properties of toughened epoxy resins with pre-formed thermoplastic polymer particles

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## ABSTRACT

The aim of this study is to characterize the adhesive properties of the toughened epoxy resins blended with pre-formed polyamide-12 particles in comparison with conventional approach using core-shell rubber particles. Dicyandiamide (DICY) cured diglycidyl ether of bisphenol-A was used as the base epoxy resin. T-peel adhesive strength of the toughened resin including 20phr polyamide-12 particles was about 3-times as strong as that of the non-modified resin. In the case of rubber toughening, the improvement in adhesive strength tended to saturate to a certain level, even with improving in the resin toughness itself. Polyamide particles embedded in epoxy resin matrix were fractured after the large plastic deformation during the peel process, which suggested the crack bridging mechanism by the particles worked behind the crack tip. The crack-wake toughening using the pre-formed thermoplastic polymer particles would hardly get the constraint effect to the deformation by the existence of rigid metal adherends. Therefore, the toughening mechanism is promising to utilize the bulk resin toughness for the peel adhesive strength even in the case with thin adhesive layer between adherends.

## 1. INTRODUCTION

Structural adhesives need a good balance of peel strength, shear strength and heat resistance. Well-known conventional approach to improve the peel adhesive properties of epoxy resins is to toughen the resins by incorporating dispersed elastomeric phases. The rubber toughening mechanism has been discussed elsewhere [1-6], usually involves enhanced localized shear yielding of the epoxy matrix itself. It is logical that as the crosslink density of the matrix resins becomes greater, the toughening effect of rubber addition reduces. Therefore, this rubber toughening approach often compromises high temperature performances of the adhesive parts. One promising toughening approach for brittle epoxy resins which have high temperature performances is addition of pre-formed polymer particles [7, 8]. The aim of this study is to characterize the adhesive properties of the toughened epoxy resins blended with pre-formed thermoplastic polymer particles in comparison with conventional approach using core-shell rubber particles.

## 2. RESULTS & DISCUSSION

Pre-formed polyamide-12 spherical particles having 6 $\mu$ m average diameter (SP500 manufactured by Toray Industries, Inc.) were used as the toughening modifier because of the good adhesion with epoxy resins and the intrinsic toughness. Dicyandiamide (DICY) cured diglycidyl ether of bisphenol-A (DGEBA) was used as the base epoxy resin. In detail, two types of DGEBA having different molecular weights were used in form of the mixture of them. Each product designation was Ep828 and Ep1001 manufactured by Japan Epoxy Resins Co., Ltd. The resin composition was set as Ep828 / Ep1001 = 40 / 60 by weight. Ep828 was a liquid type epoxy resin having an average molecular weight of 380g/mole. Ep1001 was a solid type epoxy resin having an average molecular weight of 900g/mole. 5 parts of DICY was added to 100 parts of the two resins mixture by weight. To prepare the modified resin specimens, the epoxy mixture was first heated to 120 $^{\circ}$ C to lower the viscosity of the resin, making it easier to disperse the polyamide-12 particles or core-shell rubber particles. The pre-formed particles were added slowly into the resin mixture and blended in by hand first and mechanically stirred for 1hr. After adding DICY, the resin compositions were held at 120 $^{\circ}$ C under a vacuum to degas. The resin compositions were poured into a preheated silicon-coated mold and cured at 140 $^{\circ}$ C for 2.5 hours + 150 $^{\circ}$ C for 1.5 hours + 170 $^{\circ}$ C for 1 hour. Test specimens were machined from the as cut, 6mm thick plaques.

All fracture toughness measurements of resins were conducted using a pre-cracked specimen in a compact tension configuration (Figure 1) in accordance to ASTM D 5045. The specimens were machined to a length of 40mm, a width of 40mm, and a thickness of 6mm. Two identical holes of 8.4mm diameter were drilled in the specimen as points to load in tension mode. A deep notch was first cut into the center of the specimen using a jeweler saw. A fresh razor blade, which has been chilled in liquid nitrogen, was then tapped into the tip of the notch with a hammer to create a sharp pre-crack front in the specimens.

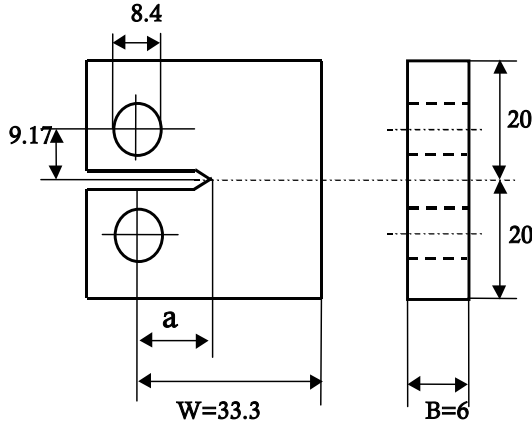


Fig.1 Specimen for the fracture toughness test (Compact Tension test) of cured resins

These specimens were then loaded in a tension mode using Intesco testing machine at a cross-head rate of 1mm/min at 25°C. The fracture toughness values,  $K_{IC}$ , of the cured resins were calculated from the following equation (1).

$$K_{IC} = (P \cdot BW^{1/2}) f(a/W) \quad (1)$$

where  $f(a/W) = (2 + a/W) \cdot 0.886 + 4.64 a/W \cdot 13.32 (a/W)^2 + 14.72 (a/W)^3 \cdot 5.6(a/W)^4 \cdot (1-a/W)^{3/2}$

, as well as P, a, B and W indicate maximum load, crack length, thickness and width of the specimen, respectively.

Adhesive specimens were prepared using aluminum adherends that had been wiped using acetone and treated with UV / ozone atmosphere to prepare the surfaces for bonding. T-peel and tensile shear adhesive properties of the specimens with / without the toughening modifiers were evaluated. Also, the effects of the bond thickness on the peel adhesive properties were examined.

Figure 2 shows the toughening effect of polyamide-12 particles in comparison with that of core-shell rubber particles. Rubber particles modification indicated higher toughening effect for the moderately crosslinked epoxy resin than polyamide-12 particles modification at the same content of modifier.

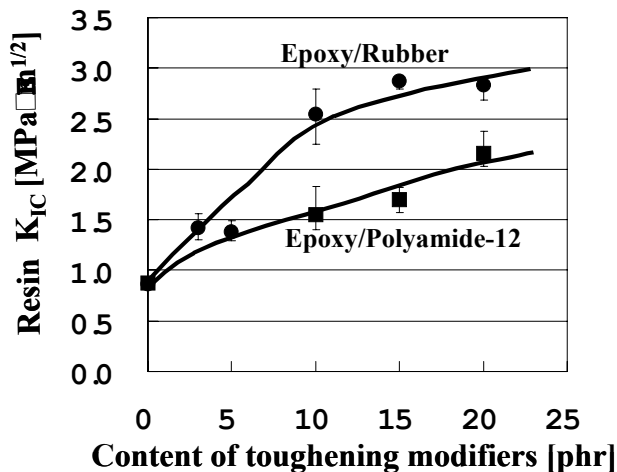
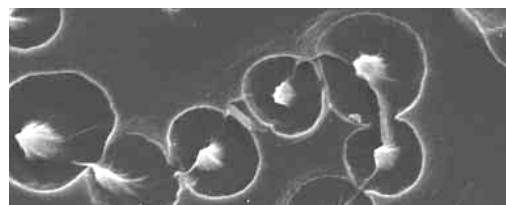


Fig.2 Improvement in fracture toughness of epoxy resins using toughening modifiers (polyamide particles, rubber particles)



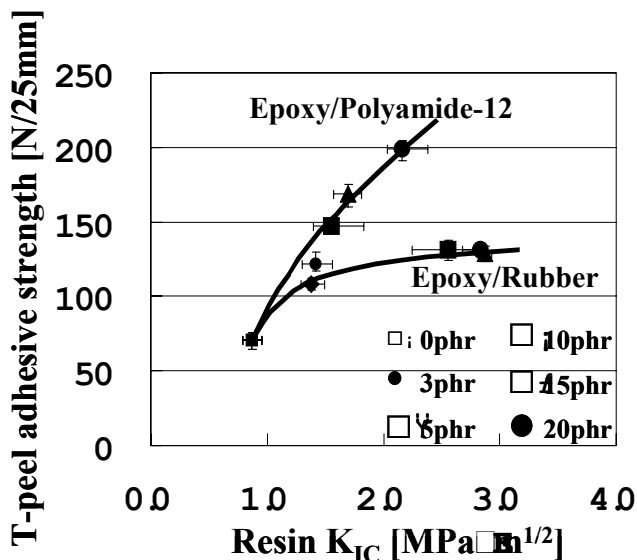
(a)Epoxy resin / core-shell rubber particles

(b)Epoxy resin / polyamide-12 particles

**Fig.3 Scanning electron micrographs of fracture surfaces (process zone) of epoxy resins with toughening modifiers from within the process zone; particle content : 20phr  
(a)core-shell rubber particles, (b)uniform polyamide-12 particles**

SEM observation (Figure 3) shows the fracture surfaces of the resins after compact tension tests. The rubber toughening system in Figure 3 (a) shows cavitation of the rubber particles and localized yielding of the epoxy matrix around the cavitated particles. The shear yielding and plastic deformation of the epoxy matrix would absorb the energy given externally, as written in several references [1-6]. On the other hand, the polyamide-12 toughening system in Figure 3 (b) shows the presence of highly drawn particles of polyamide-12 in the process zone just ahead of the pre-crack. The particles adhered well to the epoxy matrix and were capable of large plastic deformation to absorb the energy given. The large plastic deformation of particles would indicate the particles worked as “bridges” of advancing cracks until the final tearing of the particles and suppressed the crack propagation [8].

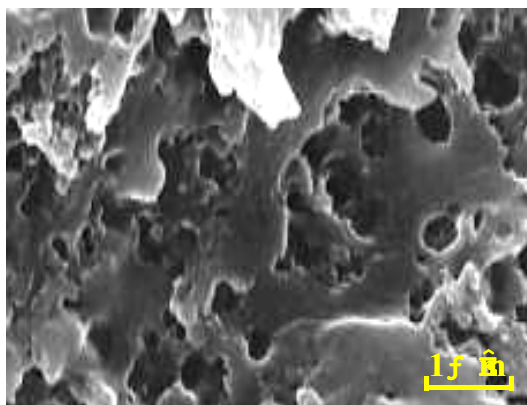
Figure 4 shows the relationship between the fracture toughness of the modified resins and the T-peel adhesive strength using the identical resins. Improved resin toughness did lead the improvement on the T-peel adhesive strength. However, the effectiveness of resin toughening for the improvement on the adhesive strength was different between rubber toughening approach and polymer-particle toughening approach. In the case of toughening using polyamide-12 particles, improved resin toughness directly led the improved T-peel strength. T-peel adhesive strength of the toughened resin including 20phr polyamide-12 particles was 200 N/25mm, which was about 3-times as strong as that of the non-modified resin.



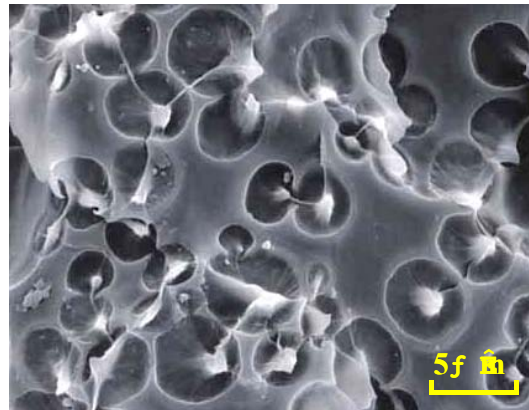
**Fig.4 Relationship between increase in T-peel adhesive strength and fracture toughness of the modified adhesive resins (modifiers : Polyamide-12 particles / core-shell rubber particles , average thickness of adhesive resin layer : 30µm)**

In the case of rubber toughening, however, the improvement on adhesive strength tended to saturate to a certain level, even improving the resin toughness itself by increasing the rubber concentration. As a result, polyamide-12 modification gave better T-peel adhesive strength than rubber modification on the equivalent resin toughness. This suggests the adhesive properties depend not only on the fracture toughness of the bulk resins but also on the deformation and fracture mechanics under the particular stress condition within the adhesive layer. Therefore, we investigated those mechanisms using microscope methods.

Figure 5 by SEM observation shows the fracture surfaces of the specimens after T-peel adhesive strength tests. The photographs show the similar fracture surfaces to the fracture surfaces of bulk resins in Figure 3. The observation indicated the polyamide particles embedded in epoxy resin matrix were fractured after large plastic deformation during the peel process.



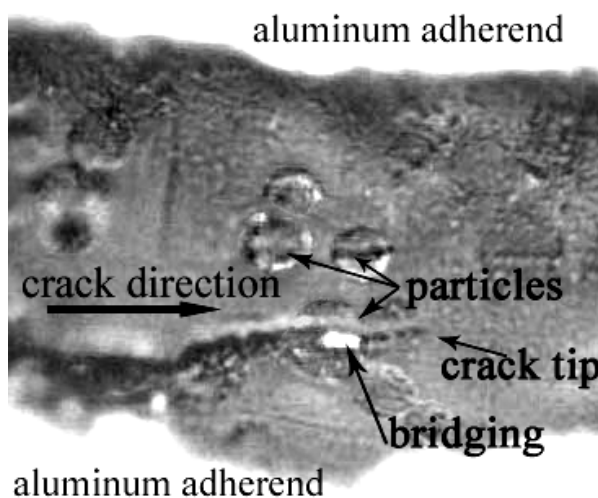
(a)Epoxy resin / core-shell rubber particles



(b)Epoxy resin / polyamide-12 particles

**Fig.5 Scanning electron micrographs of fracture surfaces of adhesive resins with toughening modifiers after T-peel adhesive tests; particle content : 20phr (a)rubber particles, (b)polyamide-12 particles**

Figure 6 is an optical micrograph which shows cross-sectional view of magnified adhesive resin layer of a specimen on the way of T-peel adhesive test process. It can be seen that a polyamide particle is bridging a loaded crack. The crack bridging by thermoplastic polymer particle works behind the crack tip and seems to prevent the crack propagation.



**Fig.6 Optical micrograph of cross-section of adhesive resin layer with polyamide-12 particles on the way of T-peel adhesive test ; particle content : 10phr**

**Note: Arrow indicates direction of crack propagation. The crack bridging by a polyamide-12 particle was observed behind the crack tip.**

The crack-wake toughening using thermoplastic polymer particles would hardly get the constraint effect to the plastic deformation by the existence of rigid metal adherends, as

schematically written in Figure 7. Because the aluminum adherends would be separating each other from the point just behind the crack tip in the peel process, constraint effect by the existence of adherends would not work on the crack-wake region. Therefore, the toughening mechanism is promising to utilize the bulk resin toughness for the peel adhesive strength even in the case with thin adhesive layer between adherends, which leads the high peel strength. This would not be the case of rubber-toughening which works in front of the crack-tip within a thin adhesive layer.

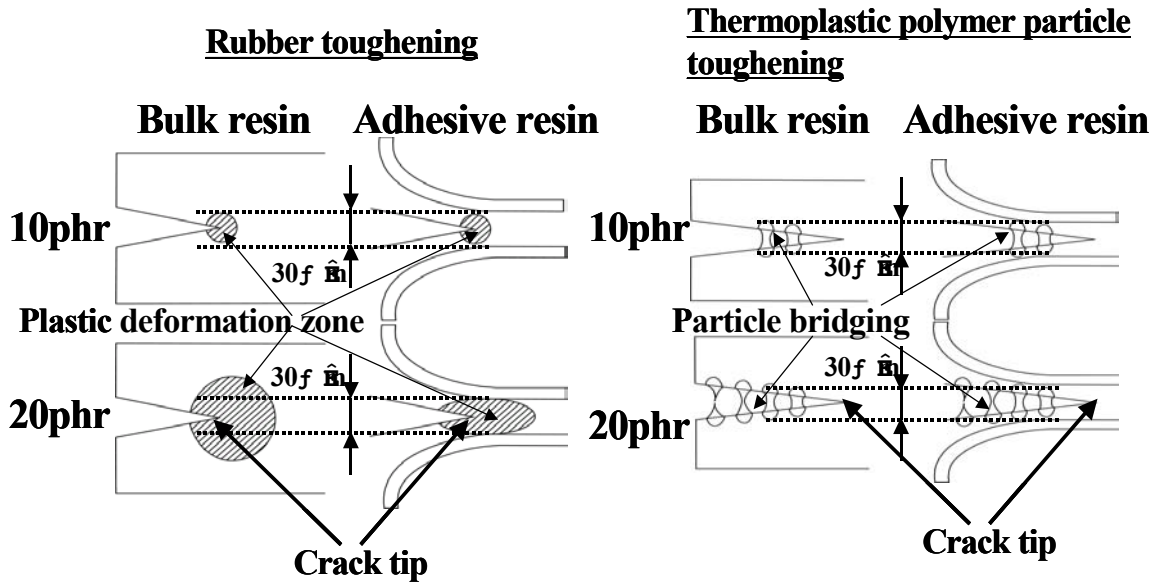


Fig.7 Estimated mechanism on increasing in T-peel adhesive strength of the modified adhesive resins and fracture toughness of the resins

In order to analyze the constraint effect of the adherends to plastic deformation of rubber-toughened epoxy resins, the size of the plastic deformation area of the resins were roughly calculated using the next Irwin's equation: (2).

$$r_p = \frac{1}{5.6f\bar{I}} \left( \frac{K_{IC}}{f\bar{D}_y} \right)^2 \quad (2)$$

where  $r_p$ ,  $K_{IC}$  and  $\bar{D}_y$  indicate the plastic deformation area (distance) from the crack tip, fracture toughness and the yield stress of the resin, respectively. The calculated values were indicated in Table 1. According to the results, the plastic deformation area size in front of the crack tip of the resin with 5 phr rubber would already reach the bond thickness (about 30  $\mu$ m) of adhesive layer. In comparison between the resin with 5 phr rubber and the resin with 15 phr rubber, increased concentration of the rubber particles enhanced the potential of plastic deformation of the resin, which would brought about the increased fracture toughness of the bulk resin.

Table 1 Calculated size of plastic deformation zone of rubber-toughened epoxy resins

Rubber contents [phr]	5	10	15	20
$K_{IC}$ [MPa $\sqrt{m}$ ]	1.38	2.55	2.87	2.83
$f\bar{D}_y$ [MPa]	62	57	50	46
$r_p$ [ $\mu$ m]	28	114	187	215

However, in adhesive specimens, the plastic deformation zone in front of the crack tip could not exceed the bond thickness of the specimen, although it would extend toward the plane direction [9]. Therefore, it would be reasonable that the peel adhesive strength tended to saturate to a certain level even improving the resin toughness itself with increasing the rubber concentration.

In this context, one can imagine there would be some effect of bond thickness on the improvement of peel strength of the rubber-toughened epoxy resin. Figure 8 verifies the effect of bond thickness on the peel adhesive strength. The reaching value of the peel strength of 100- $\mu$ m-thickness rubber-toughened system was about 170N / 25mm, which was higher than that of 30- $\mu$ m-thickness system (130N / 25mm). Increased bond thickness did lead the enhanced peel strength, which would be originated from the enhanced plastic deformation area. In the mean time, toughened system with polyamide-12 particles effectively brought about the improved T-peel strength (200N / 25mm), which exceeded the conventional rubber toughened system. The crack-wake toughening mechanism works behind the crack tip mentioned above seems to be the source of the high peel strength. Almost no influence of bond thickness could be found on the improvement of peel strength of the polyamide-toughened epoxy resin.

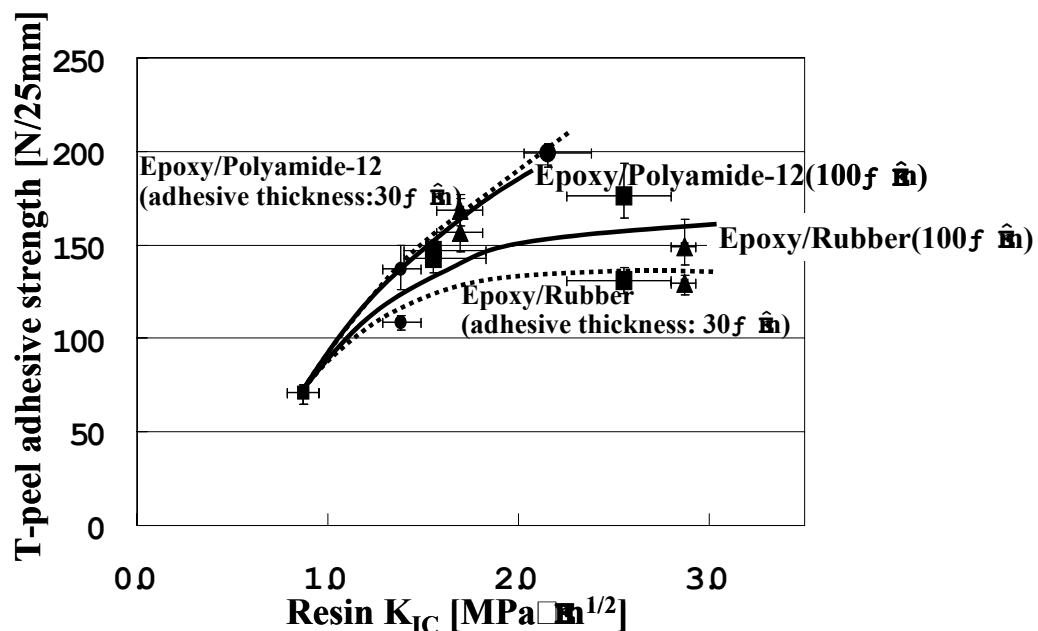


Fig.8 T-peel adhesive strength of the toughened adhesive resins and the dependence on thickness of adhesive resin layer (average thickness of adhesive resin layer : 30 $\mu$ m, 100 $\mu$ m)

High temperature performances and lap shear adhesive properties of the toughened epoxy resin with polyamide-12 particles were also examined. Figure 9 shows the storage modulus of the modified epoxy resin with 10phr polyamide-12 particles and that of the unmodified parent resin. The storage modulus and the glass transition temperature of the modified resin with polyamide-12 particles were very similar to that of the unmodified resin, which means the modification using a small amount of polyamide-12 preformed particles has little influence to the heat resistance of the resin.

Figure 10 shows the lap shear adhesive strength of the modified epoxy resin with several amounts of polyamide-12 particles. Within the range of 0 ~ 10 phr of polyamide-12 particles addition, the lap shear adhesive strength are almost same level. By increasing the amounts of the particles over than 15 phr, the lap shear adhesive strength was improving. The blend with pre-formed polyamide-12 particles is a promising technology which gives a good balance of peel strength, shear strength and heat resistance to epoxy resins.

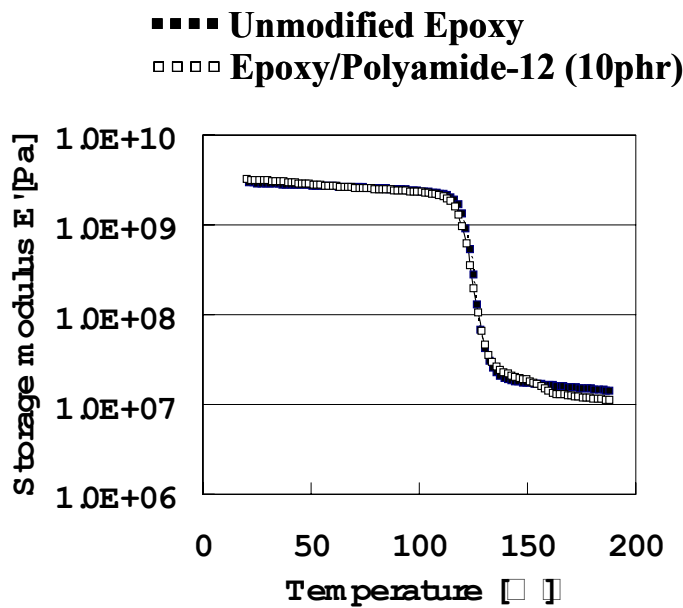


Fig.9 Temperature dependence of storage moduli of the modified epoxy resin with polyamide-12 preformed particles and the unmodified resin (parent epoxy resin : DGEBA cured by DICY)

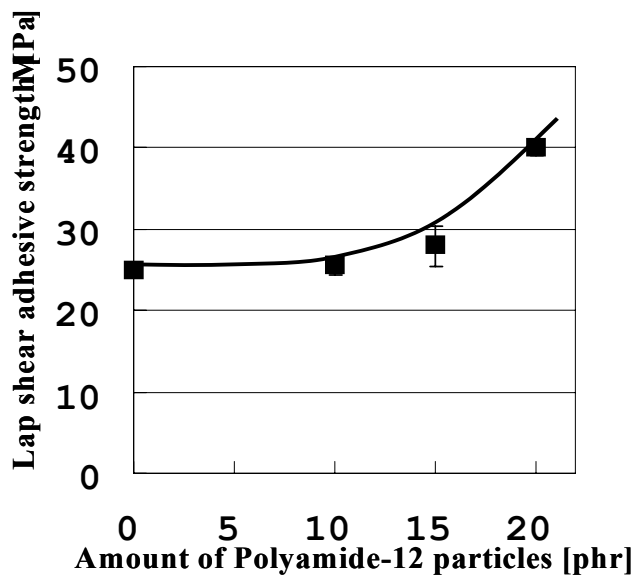


Fig.10 Lap shear adhesive strength of the toughened epoxy resins with polyamide-12 preformed particles (parent epoxy resin : DGEBA cured by DICY)

In this research, we used polyamide-12 particles as a toughening modifier. However, we do not think only polyamide-12 particles have such modification effect. From discussions mentioned above, the requirements for polymer particles which work as the modifiers using the similar bridging mechanism would be next two: (1) The particles should adhered well to the epoxy matrix. (2) The particles should possess capability of plastic deformation to absorb external energy until the final tearing of the particles.

### 3. CONCLUSIONS

- (1) The toughened epoxy resin including polyamide-12 particles performed about 3-times T-peel adhesive property as strong as that of the non-modified resin. The modified resin also kept the high heat resistance and shear adhesive strength.
- (2) On the resin using conventional rubber toughening, the improvement in adhesive strength tended to saturate to a certain level, even with improving in the resin toughness itself. Besides, the polyamide-12 particles embedded in epoxy resin matrix were fractured after the large plastic deformation during the peel process, which suggested the crack bridging mechanism by the particles worked behind the crack tip. The crack-wake toughening using the pre-formed thermoplastic polymer particles would hardly get the constraint

effect to the deformation by the existence of rigid metal adherends. Therefore, the new toughening system could utilize the bulk resin toughness effectively for the peel adhesive strength.

- (3) The requirements for polymer particles which work as modifiers using the bridging mechanism would be well adhesion to the epoxy matrix and high toughness, i.e. capability of plastic deformation to absorb external energy.

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