

Morphologies and Properties of Cured Epoxy / Phenoxy Blends for Flexible Printed Circuits (FPCs)

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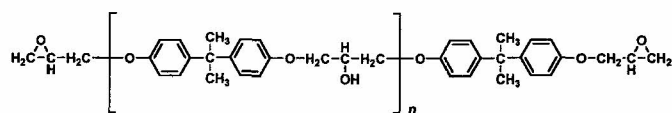
INTRODUCTION

Epoxy resins have been used widely as matrices for composite materials and as structural adhesives. However, since cured epoxy resins are brittle, the poor toughness and the low T-peel adhesion strength for disadvantages have been pointed out. The addition of rubbers to epoxy resins has been investigated in order to enhance the above disadvantageous properties of cured epoxy resins.¹⁻² While, rubber-added epoxy resins usually result in lowering the Tg. Cured epoxy containing phenoxy as one of thermoplastics has been investigated by a lot of researchers since phenoxy is a thermoplastic with a chemical structure very similar to those of high molecular-weight epoxy resins.³⁻⁷ Homogeneous and inhomogeneous epoxy/phenoxy blends can be also prepared by kinetic control of the curing rate, i.e., in the mixture of epoxy(Epon 826)/phenoxy(PHKK)/1-cyanoethyl-4-methylimidazole(CEMI) as an accelerator, when the mixture contains 0.3 or 0.5phr CEMI, the final cured product is transparent and morphologically homogeneous, while when the mixture contains 0.15phr or less CEMI, the resultant product is translucent to opaque.³⁻⁴ It was explained by kinetic and thermodynamics, i.e., when the curing rate is relatively high, the dissolved phenoxy molecules are completely locked within the epoxy networks even though the thermodynamics favor phase separation of the phenoxy, while when the curing rate is relatively low, the resultant immiscibility owing to the epoxy molecular weight increase still allows the phenoxy to diffuse and coalesce to form a separate phase.³ For the relationships between morphologies and properties, it was found that the toughness of the epoxy matrix (Epon826-DDS) will increase on increasing the amount of dissolved phenoxy, and the homogeneous blend that has the highest content of dissolved phenoxy in the epoxy matrix also possesses the highest fracture toughness, but this homogeneous blend suffers the disadvantages of having lower Tg, modulus and yield stress.⁴ On the other hand, it was also found that the DDS-cured epoxy(Epon828)/phenoxy(PKHP200) blends having a two-phase morphology showed improved ductility and toughness without significantly losing other mechanical and thermal properties such as modulus, tensile-strength, Tg and heat deflection temperature.⁵

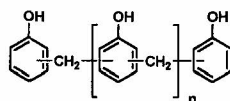
We have also been investigated the morphologies and the properties of epoxy/phenoxy blends in order to apply them to adhesives for "Flexible Printed Circuits (FPCs)". Brominated-phenoxy was used for incombustibility. The morphologies were analyzed by scanning transmission electron microscopy (STEM). For mechanical properties, dynamic mechanical analysis (DMA), tensile properties and adhesion properties were measured respectively. The adhesives for FPCs have been demanded high tensile strength and high T-peel adhesion strength without significantly decreasing elongation, lap-shear adhesion strength and Tg in order to maintain the reliability. But, since a lot of previous adhesives have been composed of epoxy/rubber blends, the rubber domains invariably resulted in significant reduction in the tensile strength, the modulus and the Tg of the composites.⁶⁻⁷ Then the reliability has not been sufficient. The aim of this study is to develop the cured epoxy composites that have high tensile strength and high T-peel adhesion strength without decreasing elongation, lap-shear adhesion strength and Tg.

EXPERIMENTAL

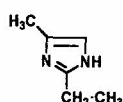
Formulations; Molecular structures of the components and the basic properties are presented in Figure1. For an epoxy, Epotohto YD-128 produced by Tohto Kasei Co., Ltd. Japan, was used. For a curing agent, novolac phenolic resin, BRG-557 produced by Showa High Polymer Co., Ltd. Japan, was used. For a curing promoter, 2-ethyl-4-methyl-imidazole, 2E4MZ produced by Shikoku Co., Ltd. Japan, was used. For a phenoxy, Phenotohto YPB-40 produced by Tohto Kasei Co., Ltd. Japan, was used. Formulations of this investigation are presented in Table1. Everyone was prepared to be a 50% with a weight varnish. For a solvent, methylethylketone (MEK) was used. An equivalent weight ratio between epoxy and novolac phenolic resin as a curing agent is 1:1.



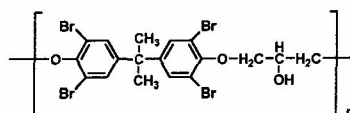
DGEBA (equipment weight of epoxy groups; 186g/eq)



Novolac phenolic resin for curing agent (equipment weight of hydroxyl groups; 105g/eq)



2-ethyl-4-methyl-imidazole for curing promoter



Brominated-phenoxy (Mw=50,000、Br content; 25% with a

Figure1 Molecular structures of components.

Table1 Formulations and properties of cured epoxy/brominated-phenoxy blends

Components and items of properties		Run-0	Run-1	Run-2	Run-3	Run-4	Run-5	Run-6	Run-7	Run-8	Run-9
Epoxy resin	Bis-phenol A type epoxy resin (YD-128)	63.6	59.3	54.8	49.9	44.6	38.9	32.5	25.6	17.9	9.5
Curing agent	Novolac type phenolic resin (BRG-557)	35.8	33.5	30.9	28.2	25.2	21.9	18.4	14.4	10.1	5.3
Curing promoter	2-methyl-4-imidazole (2E4MZ)	0.6	0.6	0.5	0.5	0.5	0.4	0.3	0.3	0.2	0.1
Modifier	Brominated-phenoxy (YPB-40)	0	6.6	13.8	21.4	29.7	38.8	48.8	59.7	71.8	85.1
Total (% with a weight)		100	100	100	100	100	100	100	100	100	100
Equivalent weight ratio between epoxy resin and curing agent		1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1
Component ratio with a weight between epoxy resin and brominated-phenoxy		100:0	90:10	80:20	70:30	60:40	50:50	40:60	30:70	20:80	10:90
Storage modulus; E' at 190°C (×10 ⁹ Pa)		2.60	2.52	2.26	1.91	1.41	0.88	—	1.00	—	—
E' at 23°C (×10 ⁹ Pa)		2.90	3.32	2.51	2.49	2.60	2.32	1.69	3.07	2.54	2.79
Glass transition temperature; Tg (°C)		154	156	152	152	154	154	—	166	—	—
		—	—	128	128	128	128	136	136	130	130
Coefficient of thermal expansion (at < Tg); α ₁ (ppm)		55	56	48	50	84	61	29	64	59	48
(at > Tg); α ₂ (ppm)		172	186	170	188	182	160	—	153	—	2122
Tensile strength (MPa)		33.3	56.6	37.8	56.1	61.7	63.8	56.5	59.6	53.4	49.1
Elongation (%)		2.1	3.9	2.7	4.0	5.3	6.9	3.3	4.1	4.0	4.4
T-peel adhesion strength (N/25mm)		3.4	3.7	3.8	4.0	5.3	7.5	7.8	9.7	10.5	12.8
Lap-shear adhesion strength (MPa)		5.4	5.1	7.9	5.8	10.1	9.5	10.7	8.3	8.0	8.1

Morphologies; A method for morphological analyses of the cured epoxy/phenoxy blends was performed by STEM. S-4700 produced by Hitachi Co., Ltd. Japan was used for a STEM instrument..

DMA and TMA; DMS 6100 produced by SEIKO Instrument Co., Ltd. Japan was used. E' and tanδ as a function of temperature were measured over -150°C-200°C. The measurements were performed at a constant frequency of 10Hz and a constant heating rate of 2°C/min. E' at rubbery plateau region gives the information of cross-linking densities of the cured epoxy/brominated-phenoxy blends and tanδ gives the information of Tg.

Tensile Tests; Tensile tests were performed to measure tensile strength and elongation of cured epoxy/brominated-phenoxy blends. For specimens, type 1 dog-bones described in JIS K 6251 that is equal to ISO 37:77 were used. The specimens were set to a tensile tester (Autograph AGS-500 produced by Shimadzu Co., Ltd., Japan), and tensile tests were performed in accordance with JIS K 7161 that is equal to ISO 527-1 at 23°C-65%RH and at a crosshead speed of 1mm/min.

Adhesion Strength; Lap-shear adhesion strength was measured in accordance with JIS K 6850 that is equal to ISO 4587:95. Copper plates (C1100P), having a size of 25mm×100mm×5mm, sanded with #200 sandpapers, were used for adherents. Epoxy/brominated-phenoxy blends for adhesives were pre-cured at 170°C-2h and then post-cured 190°C-1h. The thickness was prepared to be 0.1mm. Specimens were held to a tension test machine, Autograph AGS-500 produced by Shimadzu Co., Ltd. Japan. The test machine was run at a crosshead speed of 2mm/min in a controlled environment of 23°C-65RH%. Measurements were performed 4 times at least and the average was

adopted as lap-shear adhesion strength. T-peel adhesion strength was measured in accordance with JIS K 6854 that is equal to ISO 8510-1:90. Specimens were held to a tension test machine, Autograph AGS-500 produced by Shimadzu Co., Ltd. Japan. The tension test machine was run at a crosshead speed of 100mm/min in a controlled environment of 23°C-65RH%. Measurements were performed 4 times at least and the average was adopted as T-peel adhesion strength.

RESULTS AND DISCUSSION

Morphologies; STEM micrographs of cured epoxy/brominated-phenoxy blends are presented in Figure2. Since transmittance of electron beam at the place where bromine exists is lower than the other places, dark places showed in the micrographs would correspond to brominated-phenoxy domains. When a proportion of brominated-phenoxy for epoxy is less than 30% with a weight (Run1,2), cured epoxy phases form continuous phases. While, when a proportion of brominated-phenoxy for epoxy is over than 40% with a weight (Run5), brominated-phenoxy form continuous phases, i.e., a phase transportation takes place when a proportion of brominated-phenoxy is in 30 ~ 40% with a weight.

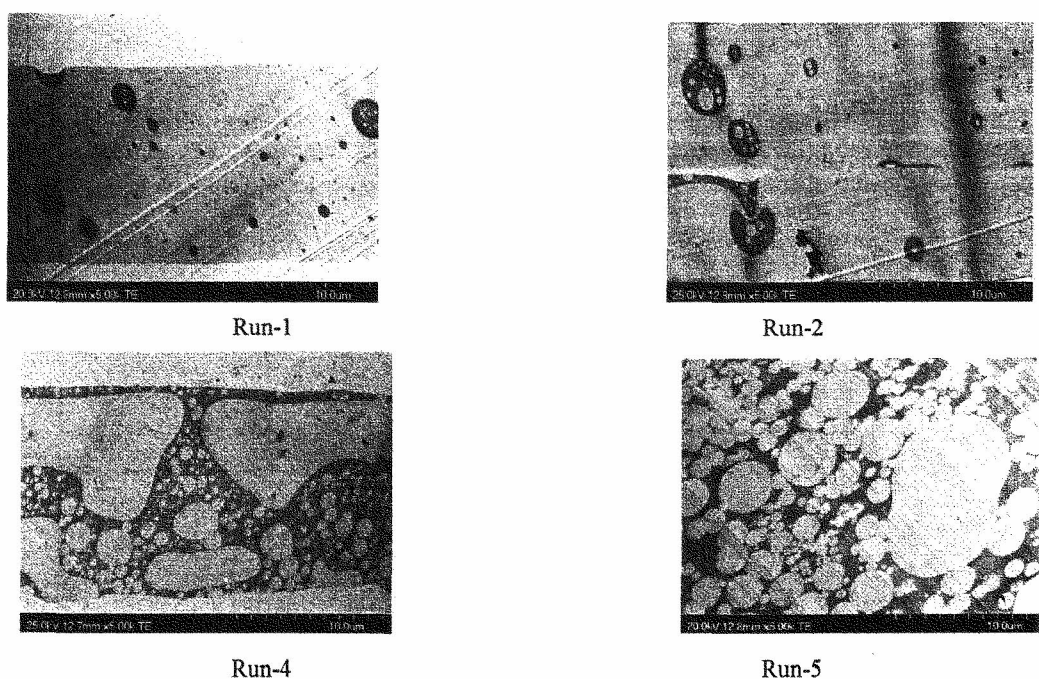


Figure2 STEM micrographs of cured epoxy/brominated-phenoxy

DMA; E' data as a function of temperature are presented in Figure3, furthermore E' data at 23°C and 190°C are presented in Table1. The decrease of E' could be due to a plasticizing effect of brominated-phenoxy. E' data at 190°C are shown as the E' values in rubbery plateaus. Generally, it is known that the cross-linking density (ρ) of cured resins is proportion to the E' in rubbery plateau as shown in equation 1.⁸

$$\rho = E' / 3\phi RT \quad (1)$$

where, ϕ is Front Coefficient, usually, that is near equal to 1. R is Gas Constant. T is absolute temperature. As shown in Figure3 and Table1, E' at the rubbery plateau region (E' at 190°C) decreased with increasing amount of brominated-phenoxy. These phenomena should be due to the unreacted brominated-phenoxy, which diluted the cross-linking densities of cured epoxies. But, even at a cured blend containing brominated-phenoxy of 50wt% for epoxy (Run5), the rubbery plateau E' still exists. So, it was found that the cured blend of Run-5 still maintains the properties due to the cross-linked matrix structures even though morphologically the continuous phases have changed to brominated-phenoxy of thermoplastics as shown in Figure1. The temperature corresponding to the maximum for α relaxation in $\tan\delta$ was described as the glass transition temperature (T_g) in Table1. Two distinct T_g 's are found in the cured epoxy/brominated-phenoxy blends. Since higher T_g is found in 155°C, it would be attributed to a cured epoxy-rich phase. While, since lower T_g is found in 128°C, it would be attributed to a brominated-phenoxy-rich phase respectively,⁵ i.e., we found that T_g of the cured epoxy-rich phase was not decreased.

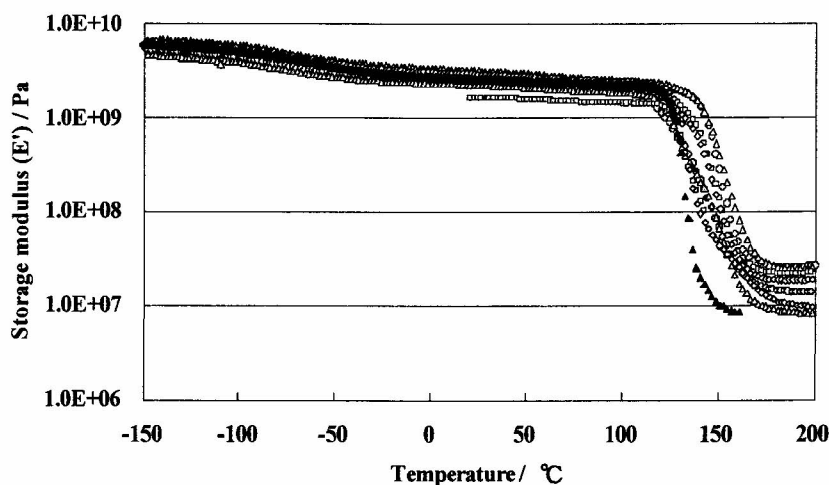


Figure3 Storage modulus(E') as a function of temperature on cured epoxy/brominated-phenoxy blends.

Tensile Tests; Tensile strength data of cured epoxy/brominated-phenoxy blends as a function of brominated-phenoxy content are presented in Figure4 and the average values are also described in Table1. Cured epoxy/brominated-phenoxy blends (Run-1 ~ Run-9) show higher tensile strength than control (Run-0).

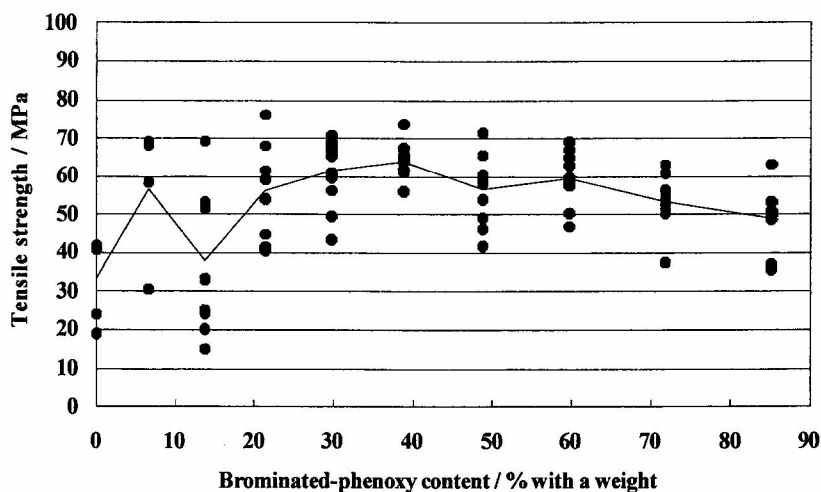


Figure4 Tensile strength as a function of phenoxy content on cured epoxy/brominated-phenoxy blends.

Tensile elongation data of cured epoxy/brominated-phenoxy blends as a function of brominated-phenoxy content are presented in Figure5 and the average values are also described in Table1. Tensile elongation data in cured blends of Run-1 ~ Run-5 are also higher than that of control (Run-0). Especially, the elongation of Run-4 and Run-5 shows a remarkable high value respectively. In Run-4 and Run-5, brominated-phenoxy domain, which is a thermoplastic, forms continuous phases as shown in Figure2. But they still have rubbery plateaus of E' as shown in Figure3, i.e., they still maintain the properties of thermosets. So, the tensile elongation would be increased by ductility due to the thermoplastic properties and the tensile strength would be increased by rigidity due to the thermoset properties.

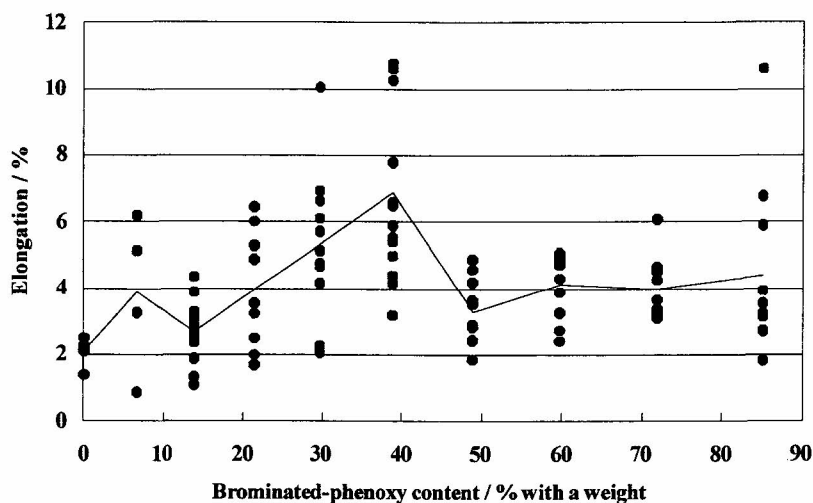


Figure5 Elongation as a function of phenoxy content on cured epoxy/brominated-phenoxy blends.

Adhesion strength; T-peel adhesion strength data of cured epoxy/brominated-phenoxy blends as a function of brominated-phenoxy content are presented in Figure6 and the average values are also described in Table1. A remarkable increase in T-peel adhesion is found in Run-4 ~ Run-9 respectively. The fracture mode of Run-0 ~ Run-3 was interfacial and that of Run-4 ~ Run-9 was cohesive respectively. Their continuous phases have converted to brominated-phenoxy from cured epoxy. Nakaya et al.⁶⁻⁷ also found that peel adhesion strength of cured epoxy/phenoxy blends increased more as the phenoxy content increased more. They mentioned that the increased peel strength is due to a good wetting property of phenoxy to copper.⁶⁻⁷

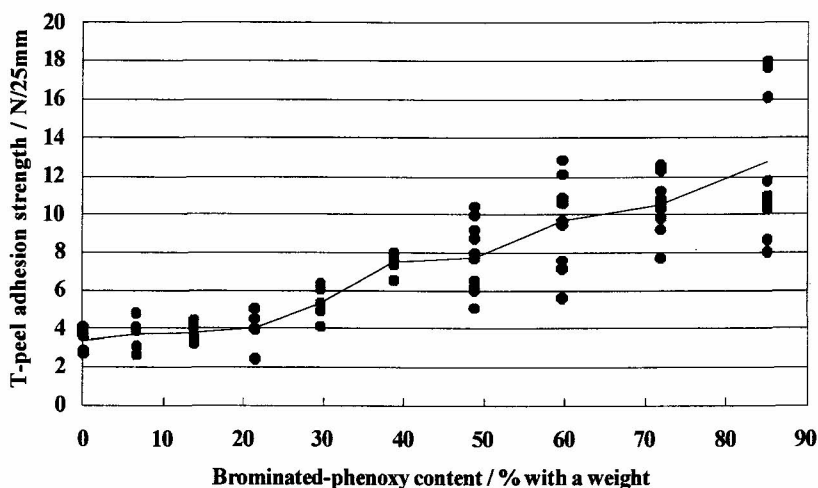


Figure6 T-peel adhesion strength as a function of phenoxy content on cured epoxy/brominated-phenoxy blends.

Lap-shear adhesion strength data of cured epoxy/brominated-phenoxy blends as a function of brominated-phenoxy content are presented in Figure7 and the average values are also described in Table1. In Run-4 and Run-5, it was found that not only T-peel adhesion but also lap-shear adhesion increases. As mentioned above, in Run-4 and Run-5, both properties of ductility derived from thermoplastics and rigidity derived from thermosets were found together. Hatano, Y., Tomita, B. and Mizumachi, H.⁹ had been investigated into viscoelastic properties of epoxy resin (Epikote828/Epikote871+Diethylenetriamine) and they found as follows. When the adhesive of the epoxy is too ductile, high values of adhesive strength are not obtained because the molecular cohesion of the cured epoxies becomes very low in this state. On the other hand, when the adhesive is too rigid, high values of adhesive strength are also not obtained because interfacial fracture occurs. Maximum adhesive strength could be obtained when the adhesive of the epoxy is not too ductile and not too rigid, i.e., the E' is 0.15-1.5Gpa.¹⁰

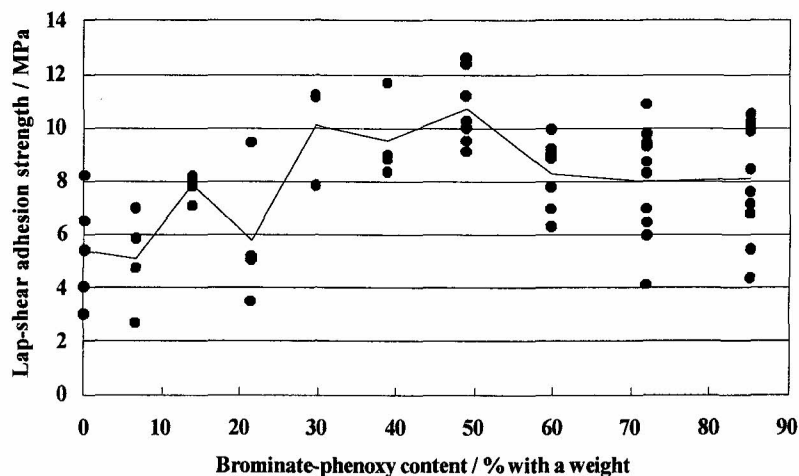


Figure7 Lap-shear adhesion strength as a function of brominated-phenoxy content on cured epoxy/brominated-phenoxy blends.

So, T-peel adhesion and lap-shear adhesion in this study could be also increased together by a good balance of ductility and rigidity.

CONCLUSIONS

When a proportion of compounded brominated-phenoxy for epoxy was less than 30% with a weight, cured epoxy forms a continuous phase. On the other hand, when it was over than 40% with a weight, brominated-phenoxy formed a continuous phase, i.e., a phase transportation took place at the brominated-phenoxy content of 30 ~ 40% with a weight. Two distinct T_g 's were found in all cured epoxy/brominated-phenoxy blends. Since higher T_g was shown in 150°C, it would be attributed to cured epoxy phases, i.e., T_g of cured epoxy was not decreased. Although brominated-phenoxy formed a continuous phase when brominated-phenoxy content for epoxy was 40 ~ 50% with a weight, the E' values in the cured blends still have rubbery plateaus, i.e., the cured blends would not have only thermoplastic properties but also thermoset properties. As the results, the tensile elongation and the tensile strength could be increased together, furthermore, the T-peel adhesion strength could be increased without decreasing the lap-shear adhesion strength and T_g .

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