

# SOL-GEL SYNTHESIS OF A DIEPOXY-CROSSLINKED ORMOCER ADHESIVE FOR Cu/POLYIMIDE SEALING SYSTEMS

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## 1. ABSTRACT

Sol-gel-derived Omocer adhesives starting from methyl-vinyl silanes, diphenyl silanes and tetraethoxy silanes with tailored strain dissipation properties have been synthesized and tailored as hot-melt sealing adhesives for Cu to polyimide. In order to establish an appropriate strain dissipation mechanism within the brittle Ormocer systems used as starting materials, an organic polymer chain based crosslinking reaction, linking amino groupings bonded to silanes together with difunctional epoxides was investigated. For controlling the process, spectroscopic data were used and correlated to peel strength. The system shows a peel strength of 10 N/cm, good dielectric properties and a high heat stability.

## 2. INTRODUCTION

Laminates of copper and polyimide are widely used in the electronic industry, e.g. as substrates for the TAB (Tape Automatic Bonding) process. Due to the very different surfaces of copper and polyimide, tailored adhesives with a high peel strength, good dielectric properties, high heat resistance and good stability against usual solvents are required. The state of the art in this field are adhesives based on acrylates [1], cyanuric acid esters [2], epoxides [3 - 5] and silicones [6]. Adhesives based on silicones show very good dielectric properties ( $\tan\delta = 10^{-3}$ ,  $\epsilon = 3$ ,  $R = 10^{13} \Omega/\text{cm}$ ) and high thermal stability, but show a rather low peel strength (3 N/cm). Advantages of the organic polymer-based adhesives are higher peel strengths up to values of 22 N/cm for epoxy-based materials, but the thermal stability is rather low. As a base line for the material development of inorganic-organic sol-gel composites for a copper polyimide adhesive, a basic inorganic-organic

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nanocomposite material described elsewhere [7], which is based on diphenyl dichlorosilane, ethyl vinyl dichlorosilane and tetra ethoxy silane as starting compounds was investigated.

### 3. EXPERIMENTAL

The Ormocer adhesive was prepared by the following route: A mixture of 69.63 g (27.5 mol%)  $\text{Ph}_2\text{SiCl}_2$ ; 98.75 g (70 mol%)  $\text{MeViSiCl}_2$  and 5.2 g  $\text{Si}(\text{OEt})_4$  [TEOS] (2.5 mol%) was given to 200 ml of boiling ethanol via a dropping funnel. After 2 h under reflux the solvent was distilled off at 70 °C and 40 mbar. The distillation residue was diluted again with ethanol and distilled off a second time. This process was repeated till the pH-value of the distillation residue was  $\geq 4$ . The yellowish resin was diluted with acetone (1 : 1) and 73.8 ml of 0.1 n HCl was added under reflux. After 3 hours reflux the acetone was distilled off at 70 °C and 40 mbar. This process was repeated twice after dilution of the residue with the same volume of acetone. The white residue was heated at 180 °C and 40 mbar for 2 hours ( $\equiv$  precondensate). The resulting yellowish honeylike resin was heated up to 230 °C in an open vessel till the following IR absorbance values, which had been determined empirically in [7], were reached:  $E_{3620}/E_{3070} = 0.18 \pm 0.01$  and  $E_{3400}/E_{3070} < 0.05$  (E = absorbance; index indicates wave number). The resulting resin at room temperature showed a high viscous consistence (hot melt) and was not able to be poured. The lamination of the foils was carried out at 110 °C.

Ormocer-epoxy hybrid system hot melt: the above prepared precondensate was treated at 180 °C and 40 mbar till the extinction ratios ( $E_{3620}/E_{3070} = 0.358 \pm 0.03$  and  $E_{3400}/E_{3070} = 0.624 \pm 0.06$ ) were reached. 30 wt% of methyl aminopropyl diethoxysilane (AMDES) was added at 140 °C to the Ormocer precondensate. The cocondensation was finished after 30 min. at 140 °C. The material was reacted with an epoxide (Araldit Gy266), based on bisphenol A, in the molar ratio 2 to 1 referred to methyl aminopropyl diethoxysilane. The reaction mixture was treated at 140 °C till the viscosity showed a thixotropic behaviour.

The peel strength was measured in a 90° peel test with a constant speed of 5 mm/min. The adhesive thickness was  $28 \pm 2 \mu\text{m}$ , respectively. The viscosity was measured by a cone/plate viscosimeter (type: KP21) at 50 °C with a constant shear rate of  $50 \text{ s}^{-1}$ .

## 4. RESULTS

In former investigations, a hot melt system for the lamination of aluminium foils with glass containers [7] has been developed. This material, starting from methyl vinyl silane, diphenyl silane and tetraethoxy silane is used as a base line for the development of a copper/polyimide adhesive. Fig. 1 shows the structural elements of the adhesive, with linear polysiloxane chains formed by the difunctional silanes (thermoplastic behavior), which were three-dimensionally crosslinked by the tetrafunctional tetraalkoxy silane.

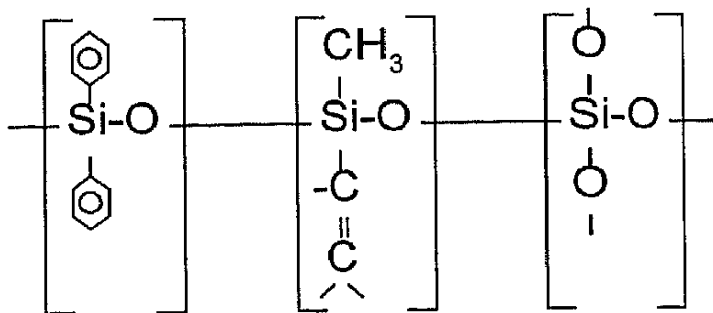


Fig. 1: Structural elements of the thermoplastic adhesive [7].

The composition of the base system for the lamination of copper to polyimide was varied systematically and correlated to the peel strength and hardness of the adhesive. In fig. 2 the peel strength and the hardness of the system with the variation of the ratio  $\text{MiViSiO}; \text{Ph}_2\text{SiO}$  is shown.

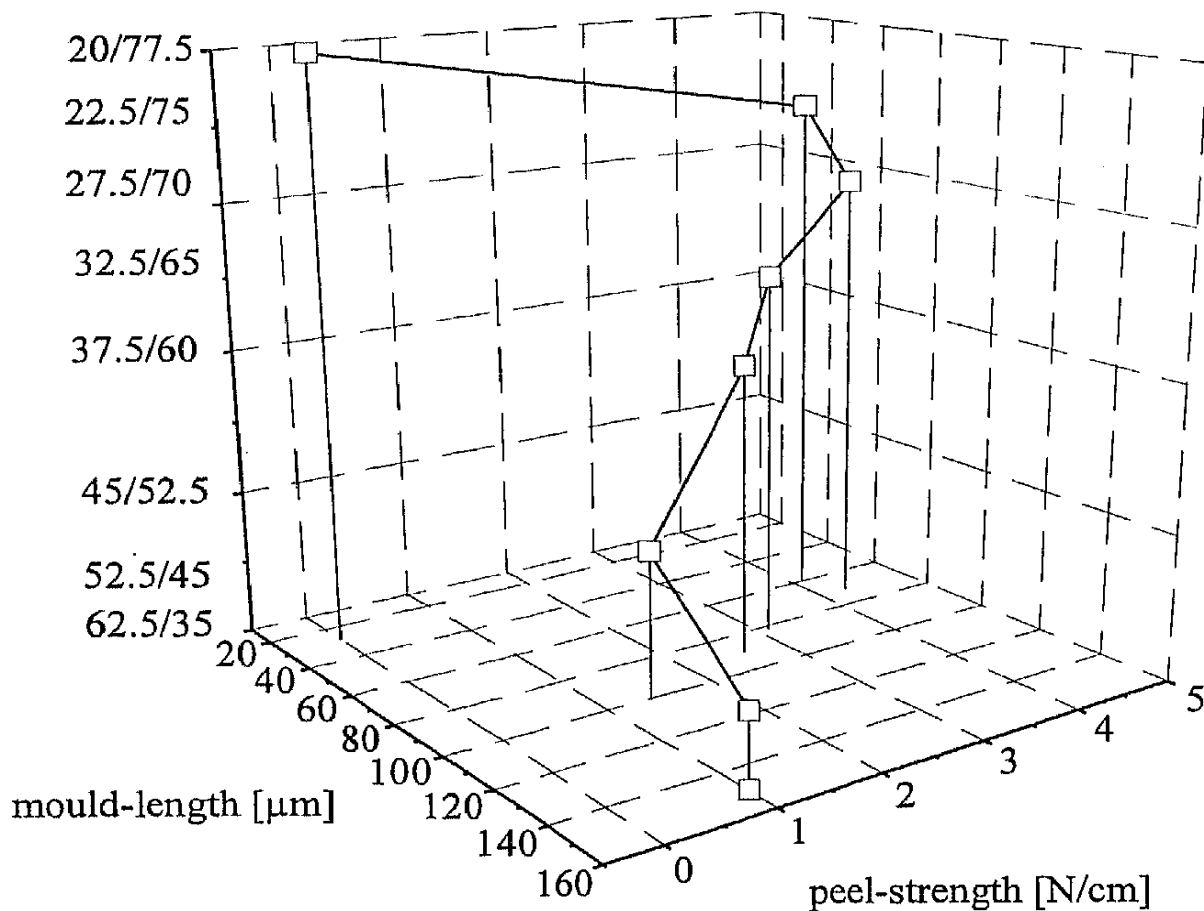


Fig. 2: Peel strength and mould length (hardness) depending on the composition Ph<sub>2</sub>SiO/MeViSiO 2.5 mole % TEOS (hardness: mould length measured after 5 s of a Vickers indentation).

With decreasing amounts of Ph<sub>2</sub>SiO (constant TEOS amount) the hardness of the system increases (decreasing mould-length). This is due to the increase of elasticity by increasing amounts of the bulky phenyl groups. Structural investigations by <sup>13</sup>C-NMR measurements show, that under the used reaction conditions no polymerisation of the vinyl groups of MeViSiO could be detected [8]. The peel strength increases with increasing amounts of MeViSiO and runs through a maximum (4.3 N/cm) with 70 mole % MeViSiO. Exceeding the value of 70 mole % MeViSiO the peel strength decreases due to the increased brittleness and thereby decreased stress dissipation ability during peel tests, proven by typical platelet structures visible in SEM micrographs of the cohesion failures of the laminates [9]. In order to increase the elasticity and thereby the stress dissipation ability of the adhesive, the incorporation of short organic chains linked to the inorganic

backbone of the adhesive was investigated. Therefore aminopropyl methyl diethoxysilane was added to a precondensate of MeViSiO, Ph<sub>2</sub>SiO and TEOS. The amino functions are used for the linkage to diepoxides of bisphenol-A type. The principle of crosslinking the inorganic backbone with organic chains is shown in figure 3.

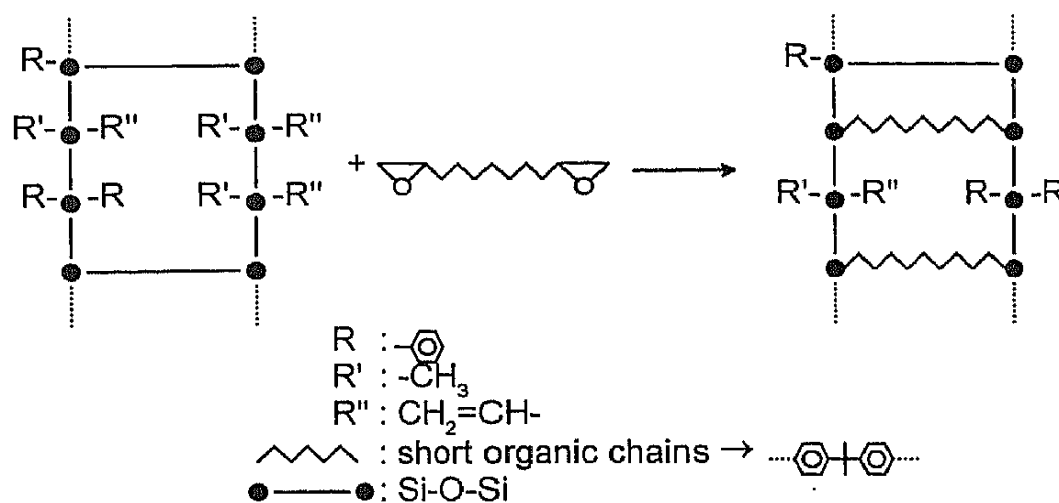


Fig. 3: Structural scheme of the increase of flexibility by incorporation of organic chains linked to the inorganic backbone.

Investigations of the concentration of AMDES and the ratio of AMDES to diepoxide show that maximum peel strength is achieved with 30 wt% amino silane at a molar ratio of 1:2 of amino silane to diepoxide if Araldit<sup>®</sup> is used. In order to find out how far the size of the diepoxide affects the sealing strength, different diepoxides were investigated. In figure 4 the dependance of increased chain length of diepoxides (epoxy equivalent) on the peel strength is shown.

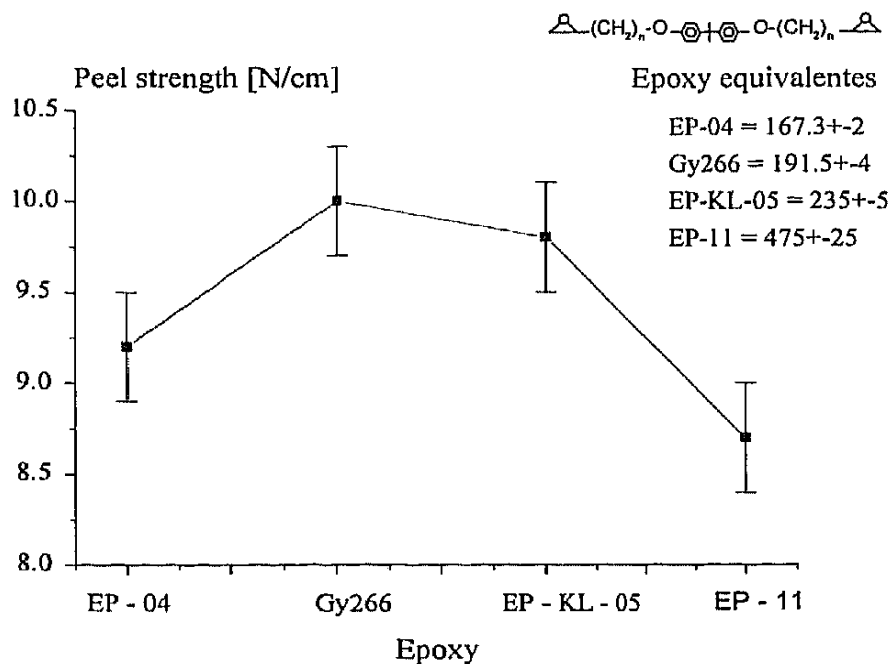


Fig. 4: Peel strengths of Ormocer systems (30 wt% aminopropyl methyl diethoxy silane; 70 mole% MeViSiO, 27.5 mole% Ph<sub>2</sub>SiO, 2.5 mole% SiO<sub>2</sub>) with diepoxides based on bisphenol A with different epoxy equivalentes in the molar ratio of 2 to 1 referred to aminosilane.

The peel strength of the adhesive with a medium chain length (epoxy equivalent 191.5) shows a maximum of 10 N/cm, a value that fulfils the needs of the electronic industry. The use of the medium chain length diepoxides for the „elastic“ crosslinking of the inorganic backbone leads to a structure with an optimum in stress dissipation ability during peel strength tests, adhesion to copper and polyimide and cohesion strength. SEM micrographs after peel tests show on the copper side a cohesion failure and on the polyimide side a mixed cohesion-adhesion failure. The SEM micrograph (figure 5) of the polyimide side show, that for this system the stress dissipation ability (elasticity) is no more the only limiting factor, but also the adhesion strength on the polyimide is equal to the cohesion strength. The typical mixed cohesion-adhesion failure is visible by the crescent shaped parts of the adhesive.

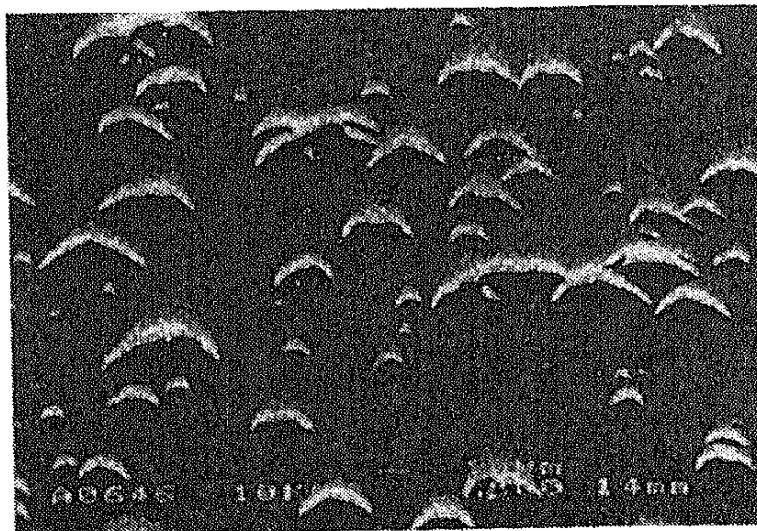


Fig. 5: SEM micrograph of the polyimide side after peel test.

The easily processable adhesive shows an excellent heat stability (180 °C; short time 300 °C), high resistance against organic solvents and good dielectric properties ( $\tan \delta = 2.8 \cdot 10^{-2}$ ,  $R = 10^9 \Omega/\text{cm}$ ,  $\varepsilon = 3.9$ ).

## 5. CONCLUSION

By short chain crosslinking of a mainly linear crosslinked ormocer adhesive based on  $\text{Ph}_2\text{SiO}$ ,  $\text{MeViSiO}$  and TEOS using amino silanes and aromatic diepoxides the stress dissipation ability and thereby the peel strength is increased up to 10 N/cm and exceeds the values for silicone based adhesives by a factor of three. Because of the shown high heat stability, good dielectric properties the easily processable ormocer adhesives is of high interest for lamination of copper to polyimide in the electronic field.

## 6. REFERENCES

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