Synthesis of High Performance Cu/Polyimide Adhesives Based on Inorganic-Organic Composite Materials

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1. Abstract

Sealing of Cu to polyimide in a hot melt process is difficult due to the very different surface properties of Cu and polyimide. Silicone-based systems are widely used due to their heat resistance, but their sealing strength is still rather low. A new hot melt system has been developed by using silane-based oligomers with polar groups (-OH and -NH_2) to provide good adhesion and aromatic epoxy units to tailor the stress dissipation ability of the system during the peel test. The system is cured by heat, shows a peel strength of 10 N/cm and is stable up to 180 °C. The synthesis principles and the general properties of the system as well as the sealing performance are described.

2. Introduction

Laminates of copper and polyimide are widely used in the electronic field as substrates for the TAB (tape-automated bonding) process. As adhesives for the lamination of copper to polyimide foils, materials with high adhesion and cohesion properties (high peel strength), high temperature stability and good dielectric properties 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 ($\tan\delta = 10^{-3}$, $\varepsilon = 3$, $R = 10^{13}$ Ω/cm) and high thermal stability, but show 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. The main reason for the low peel strength of the silicone adhesives is that the sealing medium shows a typical brittle behavior under peel stress, and the stress cannot be dissipated sufficiently in the strain zone by the system. Objective of the present investigations are the synthesis of a sol-gel-derived inorganic-organic composite with thermoplastic properties (hot melt), good dielectric properties, high thermal stability and increased peel strength in comparison to silicones by tailoring the viscoelastic properties to achieve stress dissipation properties in case of peel stress.

3. Experimental

The epoxy-modified Ormocer adhesive was prepared by the following route: A mixture of 69.63 g (27.5 mol%) Ph_2SiCl_2; 98.75 g (70 mol%) $MeViSiCl_2$ and 5.2 g $Si(OEt)_4$ [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 destillation residue was diluted again with ethanol and distilled off a second time. This process was repeated till the pH-value of the destillation residue was ≥ 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 boiled at 180 °C and 40 mbar for 2 hours. The resulted yellowish honeylike resin was heated up to 230 °C in an open vessel till the following IR-extinction ratios, which had been found empirically, were reached: $E_{3620}/E_{3070} = 0.18 \pm 0.01$ and $E_{3400}/E_{3070} < 0.05$.The resulting resin at room temperature showed a high viscous consistence (hot melt) and was not able to pour. The lamination of the foils was done 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 ± 2 µm, respectively. The viscosity was measured by a cone/plate viscosimeter (type: KP21) at 50 °C with a constant shear rate of 50 s^{-1}.

4. Results and Discussion

4.1 Material Development

In previous investigations [7], a hot seal system has been developed by sol-gel techniques starting from diphenyl silanes, methyl vinyl silanes and tetraalkoxy

silanes $(C_6H_5)_2SiX_2$, $CH_3(H_2C{=}CH)SiX_2$, SiX_4; x = OR, Cl), used for sealing of aluminium foils to glass containers. These solvent-free materials show an excellent wettability to various surfaces (glass, metals, polymers) as a prerequisite for good adhesion. The structural elements of the material are shown in fig. 1.

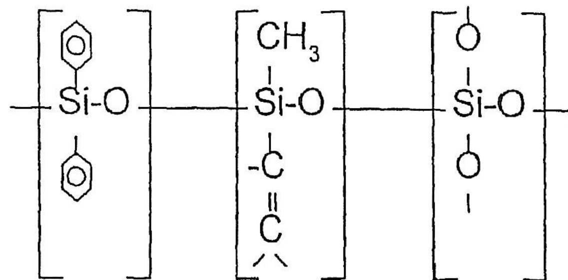
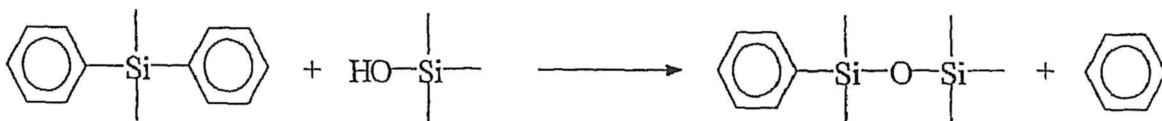


Fig. 1: Structural elements of the thermoplastic adhesive [7].

Diphenyl silanes and methyl vinyl silanes form, in general, linear polysiloxane chains, allowing thermoplastic behavior and flexibility of the material. Three-dimensional crosslinking of the inorganic backbone is achieved by condensation reactions of the tetrafunctional tetraalkoxy silane and an insertion reaction by forming a new Si-O bond, as shown in equation (1):



Both reaction paths are proved by ^{29}Si NMR. The system shows a very good adhesion to various surfaces.

The peel strength for the Cu/polyimide laminates of the basic three-component system varies with composition as shown in table 1, which can be explained by the structural differences resulting from the different number (n) of possible Si-O links for each component (I: $\phi_2SiO \rightarrow n=2-3$, II: $Si(OR)_4 \rightarrow n=4$, III: MeVi $\rightarrow$ n=2). But independent of the basic composition, the poor stress dissipation ability was the strength limiting step.

Table 1: Peel strength of Cu/polyimide laminates depending on the composition of the basic system.

Composition	$MeViSiCl_2$ [mol%]	ϕ_2SiCl_2 [mol%]	TEOS [mol%]	peel strength [N/cm)
1	30	65	5	< 0.5
2	35	62.5	2.5	< 1
3	52.5	45	2.5	1.4
4	65	32.5	2.5	3.1
5	70	27.5	2.5	4.3
6	75	22.5	2.5	4.1

In addition to this, these systems are soluble in solvents like toluene, MEK or acetone and thus does not fullfil the requirements for electronic applications. A peel strength of up to 4.3 N/cm was obtained for Cu/PI. The limiting factor was found to be the cohesion rupture, attributed to the brittleness of the system caused by a strong three-dimensional crosslinked structure of the system, as shown by ^{29}Si NMR. This lead to the concept of tailoring the structure in a way that reduced brittleness and insolubility is expected. The concept is shown in fig. 2.

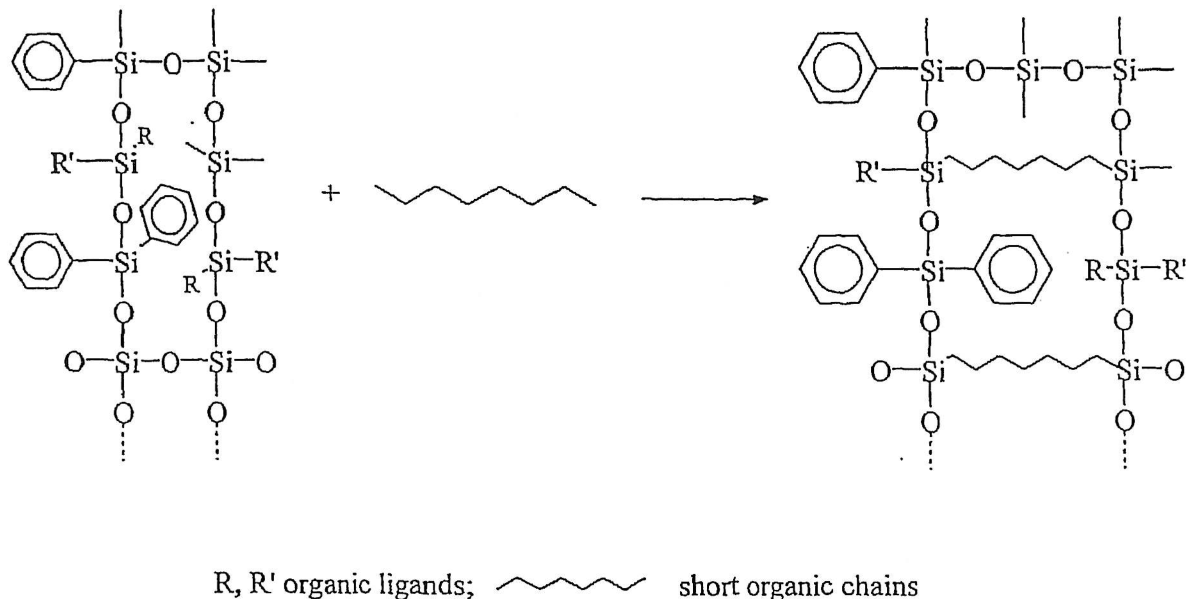


Fig. 2: Structural scheme of the increase of flexibility by incorporation of organic chains linked to the inorganic backbone.

In order to reduce the brittleness of the system as well as to increase the adhesion strength to polyimide, commercially available bisphenole-A diepoxides (Araldit®

[structure]) is incorporated as well as amino silanes (γ-aminopropyl methyl diethoxysilane) as crosslinking agents for the diepoxide. The amino silane can easily be built into the inorganic backbone by hydrolysis and condensation and can act as an adhesion promoter to PI as long as it is not consumed completely by the epoxy condensation. However, this should be able to be controlled by the synthesis chemistry. Systematic investigations showed, which are described in detail elsewhere [8], that the peel strength depends strongly on the way of the incorporation of the amino silanes ($(RO)_2(CH_3)Si/\/\/NH_2$) and decrease remarkably if no free $-NH_2$ groups are present. In the next step, the sealing strength was investigated as a function of the total concentration of the amino silane, Araldit® addition and the amino silane to Araldit ratio in order to determine the appropriate chain length according to fig. 2.

Fig. 3 shows the determined peel strength depending on the amount of incorporated amino silane and the amino/diepoxide ratio (1:1, 1:2).

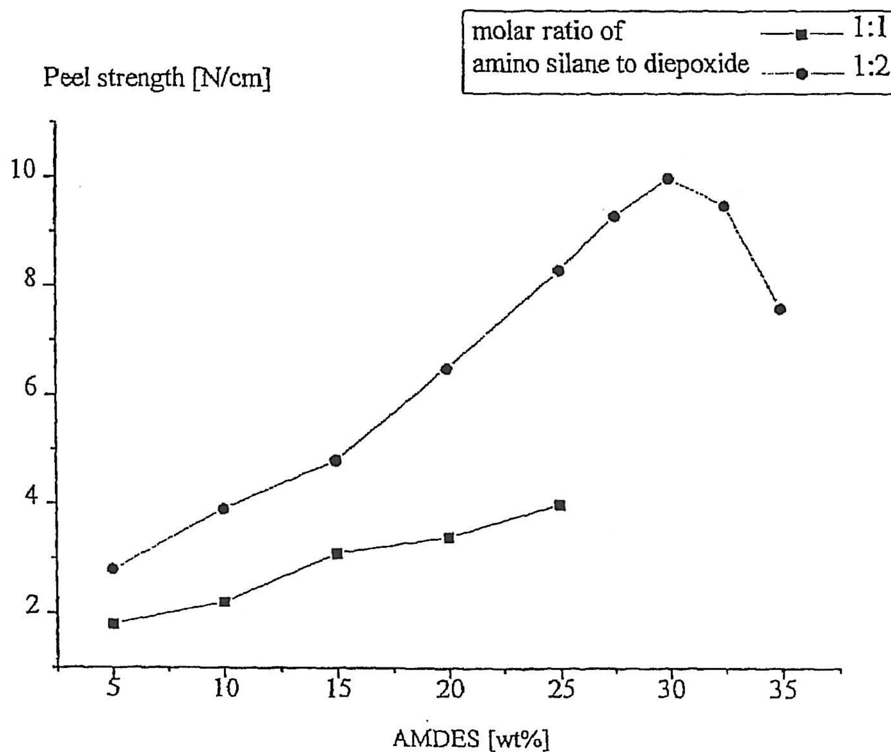


Fig. 3: Peel strengths of the aminofunctionalized Ormocer systems (70 mol% MeViSiO/27.5 mol% $(Ph)_2SiO$/2.5 mol% SiO_2) depending on the cocondensated amount of aminopropyl methyl diethoxysilane (AMDES) and the molar ratio between aminosilane to diepoxide based on bisphenol A (epoxy equivalent = 191.5)

Fig. 3 shows that the peel strength increases with the amino-to-epoxy ratio of 1:2 and shows a maximum with a total concentration of 30 wt.% amino silane. Further increase of amino/epoxy content leads to a decrease of the mechanical strength, and cohesion failures occur. ESCA investigations of the interface polyimide/adhesive show an enrichment of amino groups, which is in good agree with the determined decrease of adhesion failures at the polyimide interface. Based on these results, an optimized synthesis process is developed, which is shown in fig. 4.

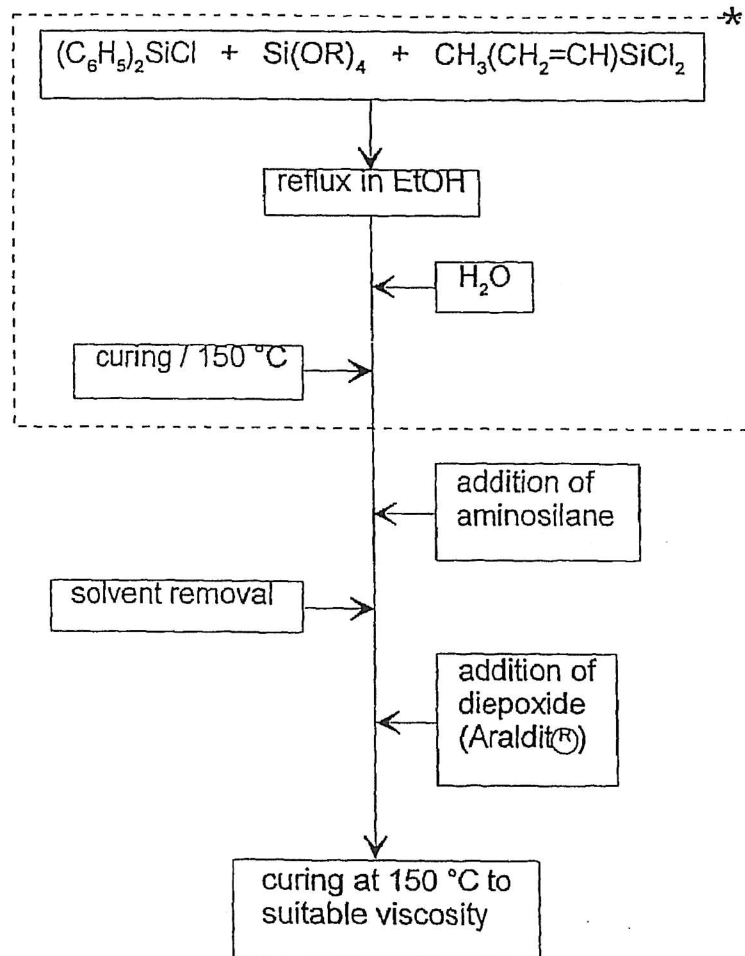


Fig. 4: Synthesis scheme of the optimized diepoxy-crosslinked inorganic-organic composite adhesive (* after [7]).

4.2 Material Properties

The preparation of the copper polyimide laminates is shown in fig. 5.

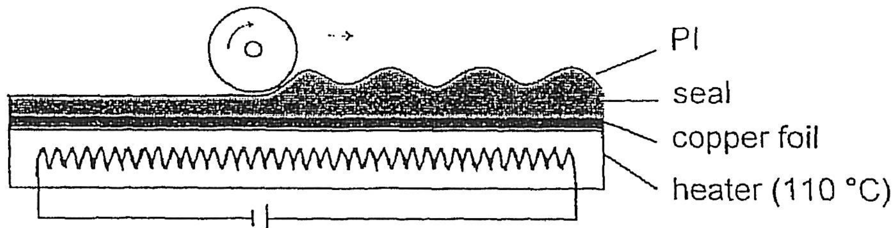


Fig. 5: Scheme of the preparation of copper polyimide laminates.

For the preparation of the laminates, the viscous hot melt adhesive is applied on the copper foil which is fixed on a heating stage (110 °C). The polyimide foil is put on the viscous adhesive. The thickness of the adhesive is easily controlled by the distance of the roller and the heated surface. The variations of the thickness of the adhesive show that a maximum peel strength is achieved with a thickness of 28 µm. The flexibility of the laminates is tested by bending to angles of -90° to + 90° with a frequency of 1 Hz, similar to DIN 50153. After 200 cycles, the copper foil cracks, but no cracks in the adhesive are visible. The failure mechanism during peel test is investigated using SEM microscopy at the surfaces of copper and polyimide. Fig. 6 shows a typical cohesion failure of the adhesive on copper.

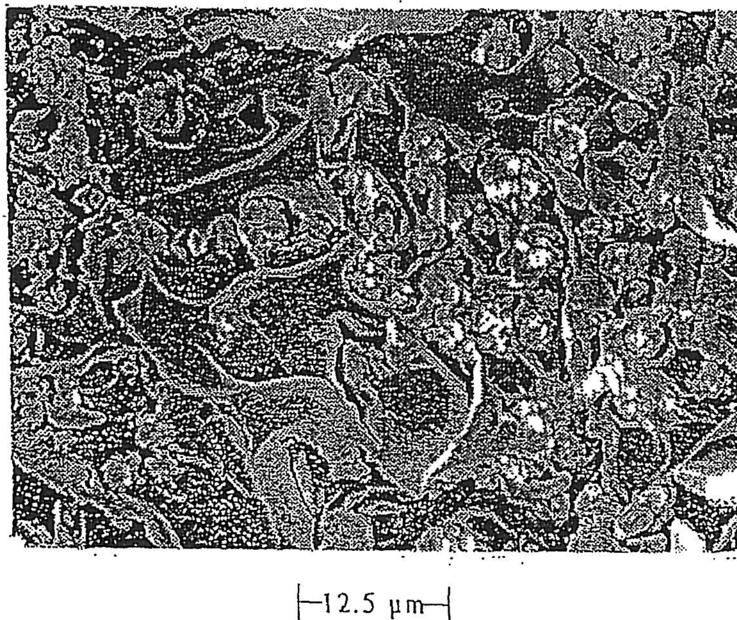


Fig. 6: SEM micrograph of a cohesion failure of the adhesive on copper.

In fig. 6 a platelet structure is visible, which is typical for cohesion failures under elastic deformation during the peel test.

The temperature stability of the adhesive is 180 °C. For testing the chemical stability of the laminates, samples are stored in ethanole, acetone, toluene, methyl ethyl ketone for 10 min at room temperature, in water for 1 month and in 5 % NaOH solution or in 5 % sulfuric acid at 50 °C for 10 min. For all cases, the laminates are stable and show no decrease in peel strength. The dielectric properties of the adhesive are shown in table 2 in comparison to a silicone adhesive [6].

Table 2: Dielectric properties and peel strength of the inorganic-organic composite adhesive compared to a silicone adhesive [6].

	surface resistance [Ω/cm]	loss factor [tanδ]	dielectric constant	peel strength [N/cm]
silicone	10^{13}	10^{-3}	3	≤ 3.5
inorganic-organic composite	10^{9}	$2.8 \cdot 10^{-2}$	3.9	10

The dielectric properties of the inorganic-organic composite adhesives are slightly lower in comparison to the silicone-based material, but fullfil the needs for electronic applications.

5. Conclusion

By tailoring of the structure of a sol-gel-derived inorganic-organic composite a hot-melt adhesive was developed for the lamination of copper to polyimide with an increased peel strength (10 N/cm) compared to usual silicone-based materials (3.5 N/cm). This result is achieved by tailoring the viscoelastic properties of the adhesive and thus an increased stress dissipation behavior during peel stress. The easily processable material shows excellent heat stability (180 °C), high resistance against usual organic solvents and good dielectric properties ($\tan\delta = 2.8 \cdot 10^{-2}$, $p = 10^{9}$ Ω/cm, breakdown voltage of $D = 10^{5}$ V/cm). Due to the shown properties, the material is of high interest for the lamination of copper to polyimide in the electronic field.

6. References

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SYNTHESIS OF HIGH PERFORMANCE CU/POLYIMIDE ADHESIVES BASED ON INORGANIC-ORGANIC COMPOSITE MATERIALS

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