Thermo-mechanical Properties of In-situ Silica Filled Silicone Resins

Pierre Chevalier, Duan-Li Ou, Yeong Lee, Steven Robson, Anne Dupont*

Summary: Silicone resins were investigated as a replacement of silica filled organic polymers for microelectronic packaging. Self-curable silicone resins containing up to 40 mol% of in-situ generated silica-like species were prepared by a novel process involving controlled hydrolysis-condensation of SiH moieties without gelation. These in-situ Q filled resins are stable and easy to process compared to post-filled organic polymers. The thermo-mechanical properties upon self-addition and condensation cure of the in-situ filled silicone resins are superior to conventional addition and condensation cured silicone resins and are in the range of organic polymers with the added advantage of high thermal and moisture resistance critical in microelectronic. Storage modulus and plateau modulus as high as 3.5 GPa with a very low fall in modulus below 5% were demonstrated. Coefficients of thermal expansion were as low as 55 to 65 ppm/K in the application temperature up to 170 °C.

Keywords: in-situ generation; IQG process; silica; silicone resins; thermo-mechanical properties

Introduction

Sealants, adhesives and packaging markets for microelectronic are largely dominated by organic resins, primarily by epoxies, as well as polyimides and polyacrylates.[1] However, recent advances in semi-conductor packaging, namely, the development of chip scale or chip size packages, have created a critical demand for high performance encapsulants. Although the coefficient of thermal expansion (CTE) of those organic polymers is low and the temperature of glass transition (Tg) in the range of 70 to 110 °C, the microelectronic packaging formulation still requires the use of silica or silicate fillers to further reduce the CTE, while enhancing the mechanical properties. However, fillers also increase the viscosity of the composition and, consequently, often reduce processability. More importantly, low moisture uptake and moisture resistance, critical in microelectronic are not fully achieved by those organic polymers.[2]

Beside the conventional organic polymers, silicones are widely employed in the electrical and electronics industries due to their unique properties, which include low alpha particle emissions, very good moisture resistance, excellent electrical insulation and thermal stability, and very high ionic purity. However, the CTE of silicone resins is high, typically in the range of 110 to 300 ppm/K, compared to 50 to 120 ppm/K for most organic polymers and have a low Tg often below 70 °C.[3]

The purpose of the present paper is to describe our latest investigation in the preparation of in-situ generated silica-filled silicone resins. These resins are stable, addition curable and are often flowable. The cured materials thereof exhibit a low CTE, high Tg and storage modulus, opening potentials for in-situ filler generation in polymer matrices for other applications.

Dow Corning S.A., Surface and Interface Solutions Center, Rue Jules Bordet, Parc Industriel Zone C, 7180 Seneffe, Belgium
E-mail: p.chevalier@dowcorning.com

Experimental

All reactions are carried out under air and in commercial solvents used as received. Spectroscopic characterization and molecular weights determination are respectively performed on a JEOL Lambda 400 MHz NMR instrument and by size exclusion chromatography in THF using polystyrene calibration standards on a coupled Waters refractive index detector. DMTA is performed on a Netzsch DMA 242 under air atmosphere. Rigid samples lapped to regular monoliths are measured at 1 Hz in three-point bending mode between −100 to 300 °C at heating rate of 2 °C/min. CTE is measured in the range of −80 °C to 240 °C on a Mettler TMA40.

Silicone Resin Synthesis

164 g (1,105 mmol) of chlorosilane precursors are mixed in 240 ml of 4-methyl-2-pentanone (MIBK) and added to a solution of 360 ml of toluene, 480 ml of MIBK and 240 ml of a 1 M HCl aqueous solution at room temperature. The mixture is refluxed under constant stirring and the organic layer is isolated and washed to neutral pH. Aqueous solution of sodium acetate is added and the mixture is heated at 70 °C overtime under constant stirring. The organic layer is isolated, washed to neutral pH and volatiles are striped off leading to silica containing resins of controlled composition, characterized by SEC, ^{29}Si and ^{13}C NMR.

Addition Cure

Silica-like filled resin are diluted in toluene and mixed with a catalytic amount of a platinum complex before casting into a mould. The mixture is gradually heated up to 200 °C for 3 h. The final free-standing film is analyzed by ^{29}Si MAS NMR, DMTA and TMA.

Thermal Post-cure

Addition-cured free-standing resin films are placed into a furnace and heated under N_2/NEt_3 vapor atmosphere at 400 °C for 2 h. Crack-free specimens are obtained for analysis by ^{29}Si MAS NMR, DMTA and TMA.

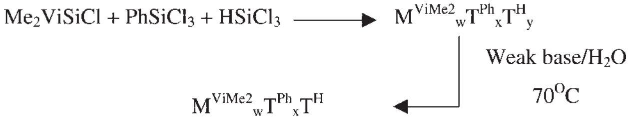
Results and Discussion

Series of $M^{ViMe2}{}_wT^{Ph}{}_xT^H{}_y$ silicone resins are synthesized by acid catalysed hydrolysis-condensation of organochlorosilanes precursors. Silica-containing silicone resins are prepared by controlled hydrolysis-condensation of the –SiH moiety into silica-like species also noted as Q sub-units,[4] according to Scheme 1 below. This process is also called IQG process (In-situ Q Generation process).

The hydrolysis-condensation rate of the –SiH moiety depends upon the mild base catalyst, its concentration and the reaction temperature. To be able to control overtime the in-situ formation of silica-like subunits within the resin structure, we have preferably used aqueous solution of sodium acetate 1 M at 70 °C.

The advantage of the IQG process over the direct formation of Q-containing silicone resins starting from e.g. tetrachlorosilane is the formation of stable silicone resins having up to 80 mol% of Q sub-units without gelation. The IQG resins are either flowable or soluble in organic solvents and cross-linkers, offering ease of processing as opposed to post-filled resins with silica fillers. Moreover, the IQG process insures the in-situ homogeneous dispersion within the resin network of silica-like species for enhanced thermo-mechanical properties.

From a wide list of investigated materials and Si-containing cross-linkers, we wish to focus here on a selection of self-addition



Scheme 1.

Table 1.
Resin compositions prepared by IQG process.

Entry	Resin composition before cure	Mw
A	$M^{ViMe2}{}_{0.23}T^{Ph}{}_{0.26}T^{H}{}_{0.42}Q_{0.09}$	2,500
B	$M^{ViMe2}{}_{0.20}T^{Ph}{}_{0.35}T^{H}{}_{0.21}Q_{0.24}$	5,200
C	$M^{ViMe2}{}_{0.22}T^{Ph}{}_{0.27}T^{H}{}_{0.15}Q_{0.36}$	6,300
D	$M^{Vi3}{}_{0.17}T^{Ph}{}_{0.30}T^{H}{}_{0.42}Q_{0.11}$	7,700

and condensation curable silicone resins to illustrate our findings.

Table 1 summarizes the silicone resin compositions we have prepared by IQG process. As expected the weight-average (Mw) molecular weight of the resins **A** to **C** increases by increasing the content of Q sub-units from 9 to 36 mol% due to cross-linking density increase and network expansion. Interestingly the resin **D** is of higher Mw due to different experimental conditions. However, those resins are more often liquid depending upon the level of silica-like sub-units.

The above silicone resins are self-addition cured forming rigid free-standing samples **A′** to **D′**. The thermo-mechanical properties of the materials: storage modulus (E'_{25}, MPa), plateau modulus (E'_p, MPa), fall in modulus between E'_{25} and E'_p ($\Delta E'$, %), and CTE (ppm/K), determined by DMTA and TMA, are reported in Table 2.

Conventional addition-cured silicone resins non-containing Q sub-units are usually exhibiting a Tg below 70 °C, a E'_{25} lower than 700 MPa with a E'_p below 50 MPa, which represents a $\Delta E'$ higher than 90%. The CTE of these traditional cured resins are usually above 130 ppm/K up to 100 °C and 300 ppm/K above 100 °C.

By comparison, the thermo-mechanical properties of the free-standing film **A′** containing only 9 mol% of in-situ generated Q sub-units are superior with a Tg in the region of 100 °C, E'_{25} and E'_p respectively above 1.8 and 0.6 GPa corresponding to a $\Delta E'$ below 70% as visualized in the DMTA curve (Figure 1).

As the content of in-situ silica increases for **B′** and **C′**, the E'_{25} slightly increases but more importantly the E'_p increases to a much higher extend, up to 1.6 GPa with a $\Delta E'$ of 25%, which is much below the $\Delta E'$ of conventional addition-cured resins. Due to the low fall in modulus for **B′** and **C′**, Tg defined by the tan δ curve is difficult to observe and is very weak compared to usual Tg of organic polymers (Figure 2).

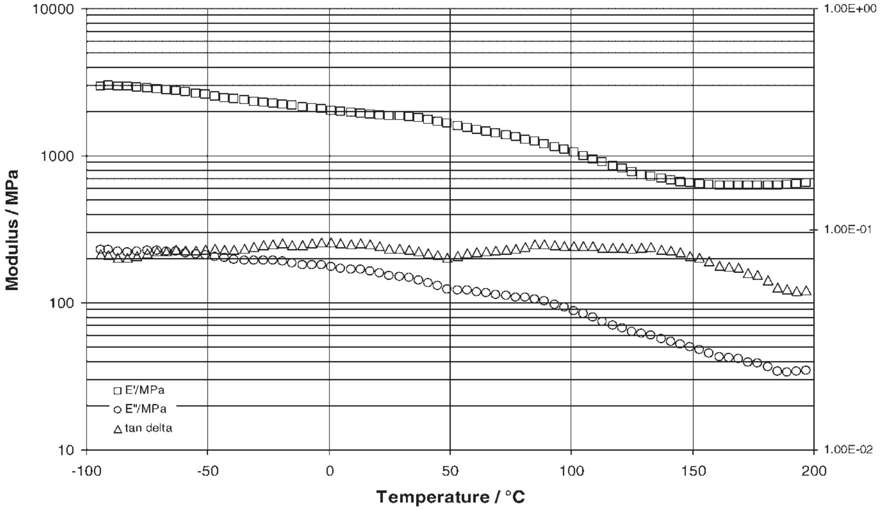


Figure 1.
DMTA of cured resin **A′**.

Table 2.
Thermo-mechanical data of self-cured and annealed resins.

Entry	E'_{25}, MPa	E'_p, MPa	$\Delta E'$, %	CTE, ppm/K (T° range)
A′	1,870	620	67	66 (−80/0), 69 (0/70), 84 (70/100), 126 (100/240)
B′	1,930	1,370	29	72 (−80/−40), 86 (−30/0), 105 (0/70), 128 (80/140), 150 (140/190)
C′	2,060	1,600	22	64 (−80/−60), 82 (−60/30), 121 (40/190)
D′	1,700	1,060	38	71 (−80/−40), 85 (−30/0), 103 (0/70), 96 (80/150), 112 (160/190)
A″	2,010	1,830	9	64 (−80/−40), 82 (−30/0), 88 (0/70), 93 (80/140), 99 (140/170)
D″	3,470	3,380	3	50 (−80/−40), 53 (−30/0), 54 (0/70), 55 (80/140), 65 (140/165)

Overall, CTE are below 120 ppm/K up to 100 °C and below 150 °C above 100 °C, which is lower than conventional addition cured silicone resins but still slightly higher than conventional organic polymers.

Within our study we also observed enhanced thermo-mechanical properties of cured IQG resins by use of polyfunctional cross-linkers. Similarly, the self-curable resin **D** has been prepared containing only 11 mol% of Q sub-units to get a flowable resin and 17 mol% of curable trifunctional M sub-units. Although the E'_{25} of the cured **D′** materials (Figure 3) is in the same range than for the cured resins **A′** of similar Q content, the E'_p is 70% higher and the $\Delta E'$ has been almost halved with no detrimental impact on the CTE.

Similarly, no clear and strong Tg could be observed. This is confirming the combined impact of a pre-formed Q containing network with the formation upon cure of “pseudo-Q” cross-linking knots. Because of remaining –SiH moieties after addition cure also due to the low reactivity of hindered T^H sub-units, a post-condensation cure treatment under N_2/NEt_3 vapor at 400 °C (annealing) is performed on both resins **A′** and **D′** leading to materials **A″** and **D″** (Table 2).

Enhanced thermo-mechanical properties are observed, not only demonstrating the thermal stability of those resins

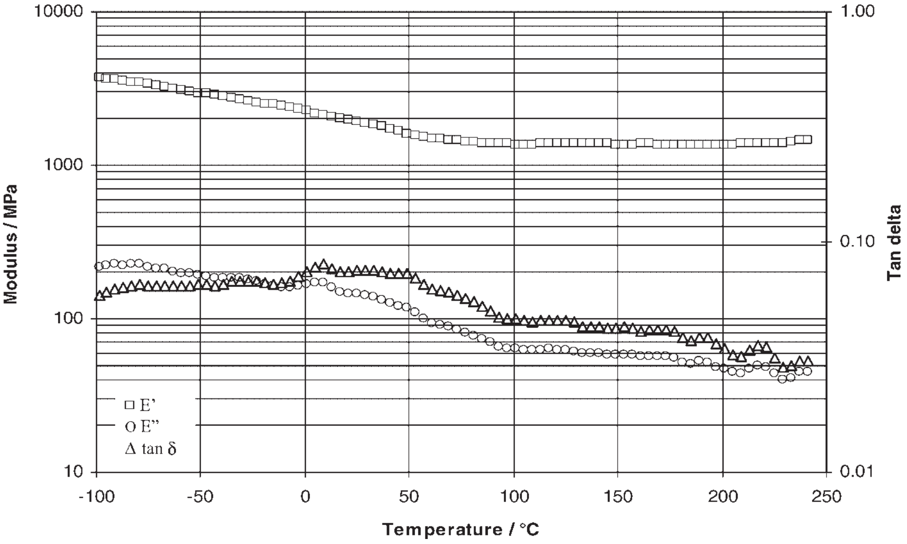


Figure 2.
DMTA of cured resin **B′**.

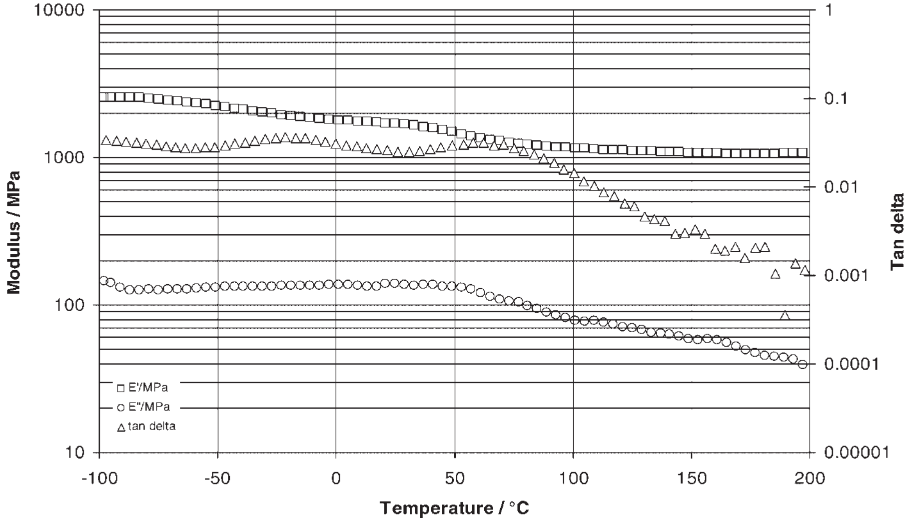


Figure 3.
DMTA of cured resin **D′**.

compared to organic resins but also revealing the very high E'_{25} up to 3.5 GPa with a $\Delta E'$ below 5%. No onset Tg and Tg up to 200 °C could be observed due to the very low $\Delta E'$ as visualised in the DMTA of the annealed material **D″** (Figure 4).

Similarly the CTE has decreased down to 55 to 65 ppm/K from 0 to 170 °C, which is now in the CTE range of most plastics.

Conclusions

Self-curable resins have been prepared by IQG process. In-situ Q filled resins are

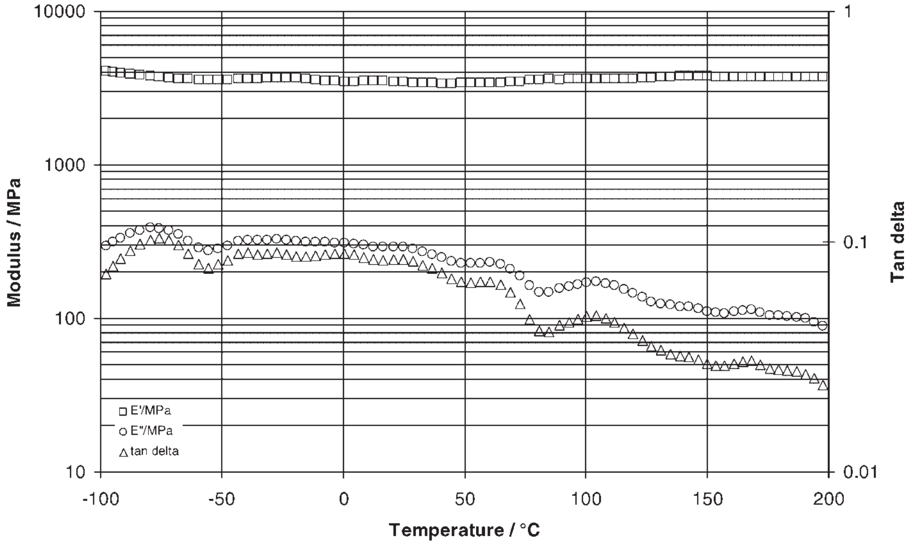


Figure 4.
DMTA of cured resin **D″**.

stable and easy to process. The thermomechanical properties upon self-addition cure and post-condensation treatment are superior to conventional addition cured silicone resins and are in the range of organic polymers with the added advantage of high thermal and moisture resistance critical in microelectronic. Extrapolation of in-situ filler technology to other polymer matrices and applications is proposed.

[1] Hitachi Cable Ltd Patent, JP 1116674 (1999)
[2] T.-H. Ho et al., *Eur. Polym. J.*, *37* (2), (2000), pp 267
[3] Dow Corning Patent, EP 1035161 (1999)
[4] Dow Corning Patent, WO 2002081552