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Research Paper

Effects of humidity, ionic contaminations and temperature on the degradation of silicone-based sealing materials used in microelectronics

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ABSTRACT

This paper investigates the effects of three ageing factors (chemical, humidity, and temperature) and their interactions on the physical properties and degradation of silicone sealant used in microelectronic applications. The thermal degradation of silicone sealants was investigated by exposing samples to temperatures in the range of 150 up to 175 °C. Also, a set of samples were aged at 40 °C in a salt spray set-up with 100 % humidity in a salty atmosphere. Results showed detectable changes in the FTIR spectra of aged specimen as compared with the as-received sample. In all accelerated testing conditions, peak intensities decreased with ageing time, inferring that that the surface characteristics of the sealant is affected by ageing. Shear test results showed that with increasing the ageing time, the maximum shear stress in most cases has decreased in all ageing conditions. Also, it appears that samples with longer ageing times have experienced more elongation before failure. Results also show that salt spraying of specimens is associated with a decrease in the mechanical properties of the sealant, indicating the deleterious implications of ionic contaminations for the mechanical properties of samples.

1. Introduction

Adhesive bonding is a key joining technology in many industrial applications, including automotive, aerospace, biomedical devices, and microelectronic components. In all cases, a reliable operation has always been the utmost priority [1–3]. Adhesive bonding is gaining more attention in the microelectronic industry due to the increasing demand for joining similar and dissimilar components, mostly within the framework of designing lightweight structures. When two materials are connected, an adequate adhesion between them is of great importance when it comes to the integrity and system reliability. Therefore, it is always important to make sure that the joint maintains its quality and its mechanical properties during service. Silicone in microelectronic devices is mostly used as an adhesive material and sealant. Silicone is known to have a rather wide service temperature range, excellent flexibility, superior electrical properties, and ability to protect components from environmental contaminants. The ability of silicone to withstand extreme environmental conditions gives it an edge over other types of adhesives and related compounds in demanding and harsh working conditions. That is why silicone is now widely used in sealing and bonding substrates in the assembly of printed circuit boards (PCBs) and other electronic modules. Silicone is the only type of adhesive that shows a perfect adherence to the PCBs substrate. Silicone can also be used for purposes other than encapsulation and adhesion. For example, electrically conductive silicone adhesives can also be used in place of solder for the attachment of some components. In addition, thermally-conductive grades can be used to bond microprocessors, LED (light emitting diode) arrays, and other heat generating components to heat sinks, ensuring an efficient path for heat transfer. Flexible silicone elastomeric coatings can be applied in a thicker layer than their epoxy counterparts providing an even higher levels of protection resistant to heat and moisture [4–7].

The focus in the present study is to understand different failure mechanisms in silicone sealants and adhesives and to see how different environmental, chemical, and service-related stresses attribute to the kinetics and extent of degradation in silicone sealants and adhesives.

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The focus will be on the degradations in microelectronic devices. The impact of different failure mechanisms on the lifetime and reliability of microelectronic devices will be methodically investigated. The main degrading factors for silicone in microelectronic applications are temperature, humidity, ionic contaminations, and mechanical loading [8]. In this investigation, the effect of the temperature on the strength and chemical stability of silicone sealants has been studied by exposing samples to temperatures in the range of 150 up to 175 °C. The effect of humidity has also been studied in controlled conditions. Mechanical failures such as cracking were also systematically evaluated. Given that severe working conditions, particularly at elevated temperatures with high levels of moisture, results in the degradation of silicone sealants, it is important to understand the interrelations between different failure mechanisms with mentioned stresses and their implications for the reliability of electronic devices. This research will be a step forward in gaining fundamental knowledge on how silicone adhesive materials in electronic packages degrade under different operational and environmental stresses.

2. Materials and method

Silicone sealant samples were synthesized based on the instruction with mixing 50 g part A with 50 g part B of the sealant. After having a homogenous sealant mixture, the sealant was put in the oven at 115 °C for 15 min, as per instruction. Aluminium plates were used as the substrate, given that it is a commonly used alloy in different applications such as gaskets and PCBs. Aluminium plates were first polished and washed with acetone in an ultrasonic set-up for 30 min, before applying the sealant layer. Sealants with the thickness of 0.25 mm (Fig. 1) were applied mechanically, using a roller blade set-up to make sure that the thickness is homogeneous. To further improve mechanical properties of sealants, extra Al_2O_3 nanoparticles at two weight percentages of 1 and 3 % were added and mixed (mechanically) with the sealant. Fig. 1 shows that the sealant has visually a rather perfect adhesion with Al substrate with no obvious indication of interfacial delamination or cracks the substrate/sealant interface.

2.1. Ageing tests

The effects of thermal ageing on sealants were studied at 150 and 175 °C. After curing at room temperature, one set of samples were thermally aged at 150 and 175 °C up to one week. The samples were then subjected to tensile and shear tests at room temperature to evaluate the implications of thermal ageing for the ductility, strength, stiffness, and bonding strength of the sealant. A set of samples were aged at 40 °C in a salt-spray set-up with 100 % humidity in a salty atmosphere. The salt spray set-up simulates harsh-environment service condition with aggressive ionic contaminations. In this case, both temperature and oxidizing ionic species come into effect, resulting in an accelerated degradation test. Samples were aged in salt-spray set-up for five days. Mechanical and chemical properties of aged samples after salt-spray test were also studied.

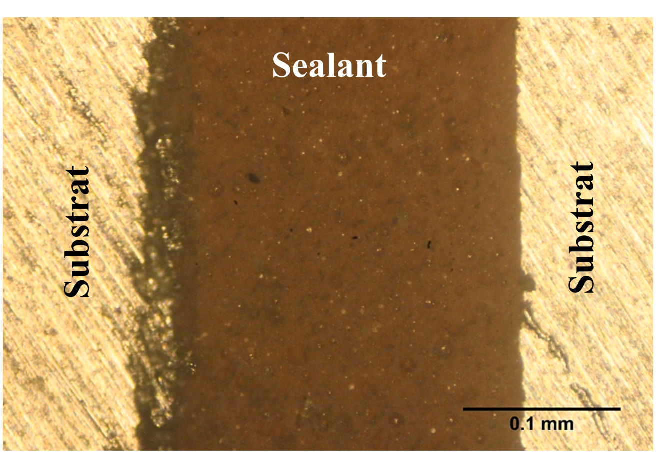

Fig. 1. Thickness of the silicone sealant layer, in between to aluminium substrates.

2.2. Mechanical testing

Tensile tests were conducted with a universal tensile testing machine to determine the bonding strength of the sealant (see Fig. 2a). To determine the shear strength of the joint, samples of 10 × 10 mm were cut and placed in a fixture, as shown in Fig. 2b and c. The lap shear test is surely a useful experimental method to characterize the adhesion strength of sealants in a shear mode loading condition. Having both tensile and shear test results, it is possible to determine which sample can offer the highest mechanical properties in both tensile and shear modes. Also, having the data from mechanical tests, one can conclude where the failure initiates: whether it is from the sealant itself or from the sealant/substrate interface.

2.3. Characterizations

Scanning electron microscope (SEM) was used to do the fractography on the fracture surface. Surface morphology of the aged samples was also analyzed with scanning electron microscopy (SEM) and stereomicroscopes. Infrared spectra were recorded using a Perkin–Elmer Spectrum 100 series spectrometer in the attenuated total reflection (ATR) mode for 200 scans at a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Mechanical properties

Mechanical properties of aged specimens were firstly evaluated given that tensile strength and displacement at breaking point are most immediate evidence of the performance of sealants [8–12]. As shown in Fig. 3, thermal ageing at 175 °C is associated with an obvious deterioration of tensile strength and maximum displacement. The same trend is also observed in samples, aged at 150 °C, i.e. the higher the thermal ageing time, the lower is the maximum tensile force/maximum displacement before complete de-bonding. So, as expected, increasing ageing time is always associated with a deterioration of tensile strength of the sealant.

Fig. 4 compares the maximum tensile strength of silicone sealant samples, aged at different ageing conditions. In all ageing conditions, increasing time is associated with the deterioration of maximum tensile strength of samples. It is noteworthy that the degradation kinetics is higher at 175 °C, as compared with that in 150 °C, implying the importance of temperature in the degradation kinetics of sealants. Interestingly, even though the temperature during the salt spray test is not so high (40 °C), the salt-sprayed samples have the highest degree of deterioration of mechanical properties with the highest kinetics of deterioration, inferring that the ionic contamination and thermal degradation have a synergetic contribution to the deterioration of mechanical properties of sealants. Also, it is noticeable that the initial deterioration of mechanical strength in salt-sprayed samples takes place at the very beginning of exposure, indicating the aggressiveness of salt-spray condition. This infers that ionic contaminations can dramatically deteriorate mechanical properties of sealants (even at comparatively low temperatures) and that their negative influences are much more than thermal stresses alone. On the other hand, it is shown that samples with 1 and 3 % of extra added Al_2O_3 nanoparticles show improved mechanical properties, when aged at 175 °C, with the 1 % addition showing the most prominent improvement in all samples, indicating that degradation kinetics can be controlled by addition of extra Al_2O_3

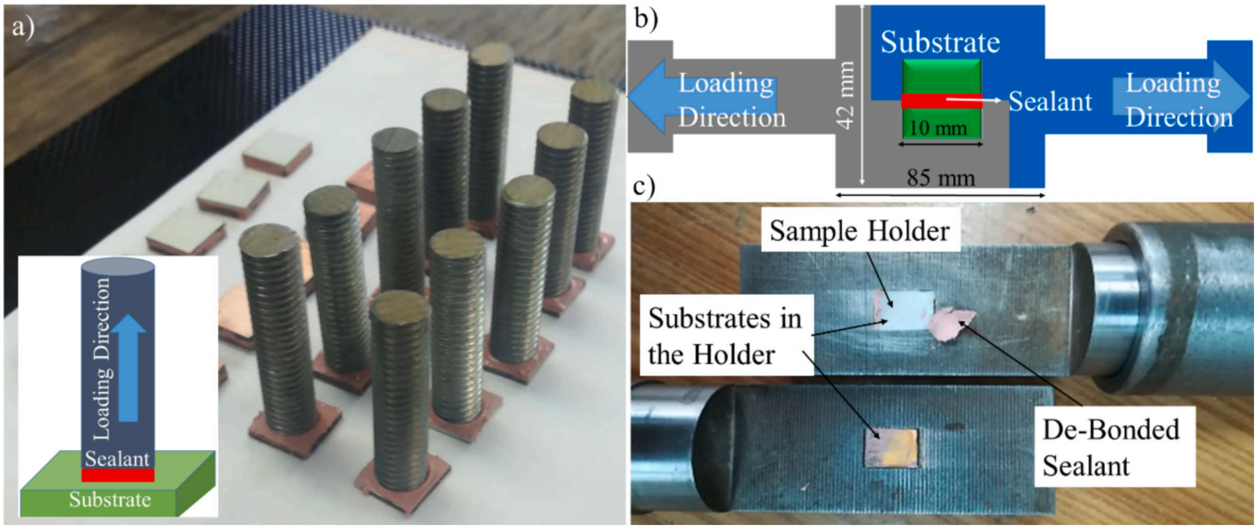

Fig. 2. Mechanical testing samples: a) Schematics of tensile test samples, b) the schematics of shear test fixture and c) shear test fixture.

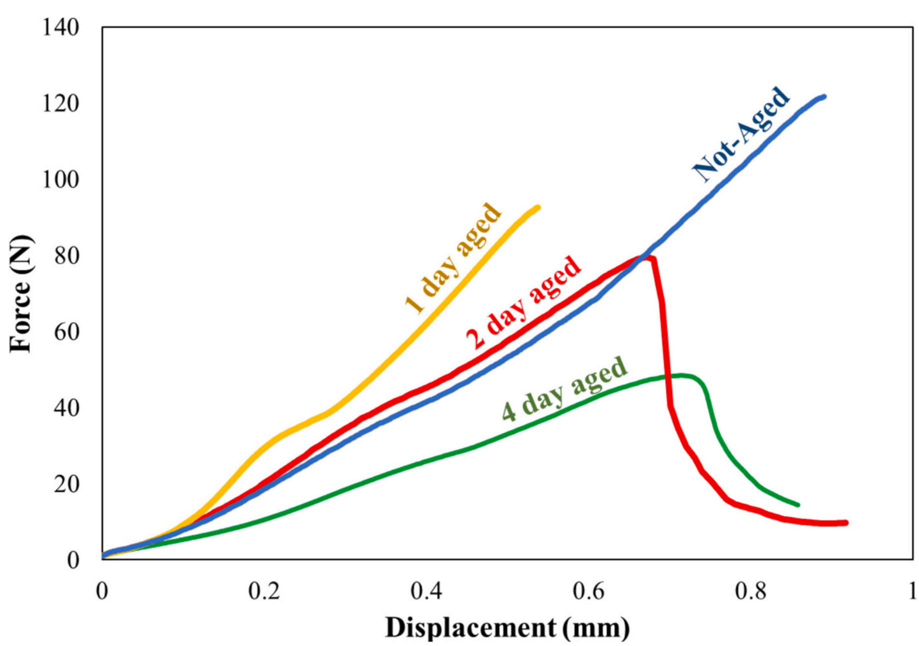

Fig. 3. Tensile strength of silicone sealant samples, aged at 175 °C, for different times.

nanoparticles.

Figs. 5 exhibits shear test data, for sample aged at 150 °C. The same arguments as tensile tests can be applied for shear strength data (as given in Fig. 3): i.e. with increasing the ageing time, the maximum shear stress in most cases decreases, though the decrease is not as much as that in the case of tensile test. Fig. 6 shows the effects of temperature and salt spray on the maximum shear strength, again confirming the deleterious effects of salt spraying on the on the mechanical properties of specimens. Similar to tensile test data, the sample with 1 % Al_2O_3 addition has the lowest kinetics of degradation, in thermal ageing condition. Minor addition of particles have always been reported to be influential when it comes to different mechanical and physical properties [13–17], which needs to be further investigated in this system.

3.2. Chemical analysis

To get a better understanding of the ageing mechanism and a reasonable evaluation, the Fourier-transform infrared spectroscopy (FTIR) analysis was also conducted. Fig. 7 represents the FTIR spectra of silicone sealants under after different ageing time at 175 °C. Three characteristic peaks for silicone rubber are observed at 1256, 1015–1085, and 795 cm^{-1}, which correspond to the vibrations of Si–CH_3, Si–O–Si, and Si–$(CH_3)_2$ bonds, respectively [18,19]. As it can be seen, there is a reduction in the FTIR spectra of aged samples as compared with as-received sample. The same trend is observed in other ageing conditions. Wavenumber 1256 cm^{-1}, is ascribed to the presence of silicon organic compounds with a methyl group. Around 1260 cm^{-1}, methyl groups attached to silicon atoms produced a distinctive deformation absorption. As the material was thermally-aged, a certain decrease in the intensity at this wavelength was found, which indicates that polymer breakages and/or oxidation of C—H bond and Si—C bond has taken place, which could promote the oxidation reactions accompanying by the formation of free radicals and oxidation products. The breakage of Si—C or/and oxidation of methyl group in Si–CH_3 are further identified by a significant decrease in the intensity of the absorption peak at 785 cm^{-1}. The obvious decreases in the intensity of the

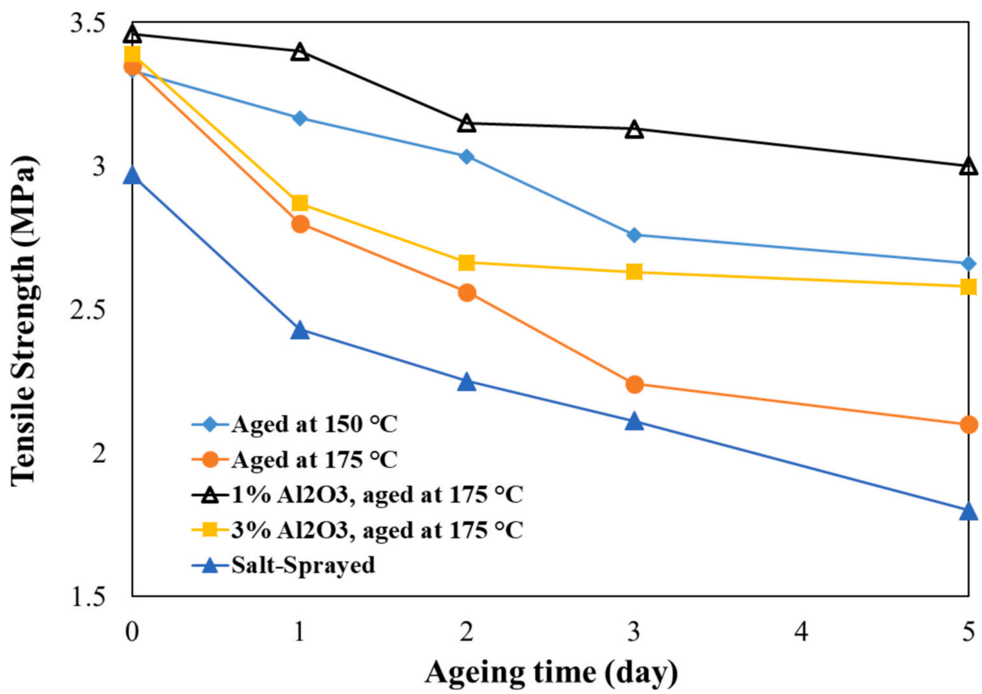

Fig. 4. Variation of maximum tensile strength of sealant samples with ageing time.

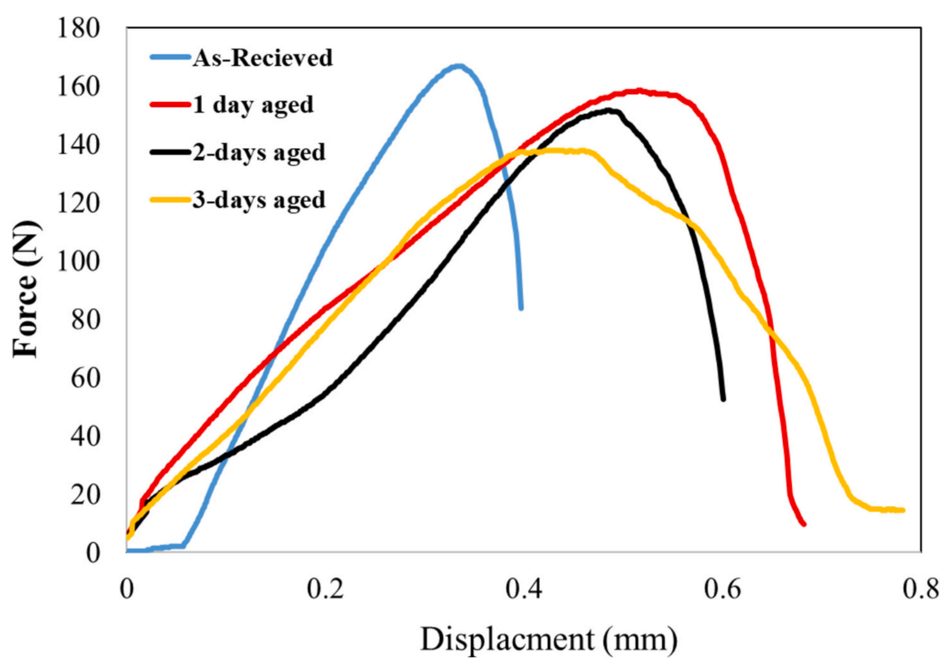

Fig. 5. Shear force vs. displacement of different ageing time at 150 °C.

absorption peaks at 1085 cm^{-1} and 1015 cm^{-1} are mostly due to the bond breakage of the Si–O–Si main chain. There is no absorption peak at 1408 cm^{-1} which indicates an integral part of rubber crosslinking network. It appears that the main chemical mechanism, controlling the degradation of sealants, is the oxidation of samples.

4. Conclusions

This paper investigates the effects of three ageing factors (temperature, humidity and ionic contaminations) and their interactions on the physical properties and degradation of silicone rubber used as sealants in microelectronic industries. Results showed that there is a detectable change in the FTIR spectra of aged samples as compared with that as-received sample. In all accelerated testing conditions, there is an overall decrease in the peak intensities with ageing time, indicating that the surface characteristics of the sealant is affected during degradation and that the oxidation appears to be an important degradation mechanism. In the shear and tensile tests it was shown that with increasing the ageing time, the maximum strength stress in all cases decreases at all ageing conditions, with the most dramatic decrease belonging to the salt-spray condition. One of the observations in the mechanical test that adding 1 % of Al_2O_3 into the sealant can have a positive implication for

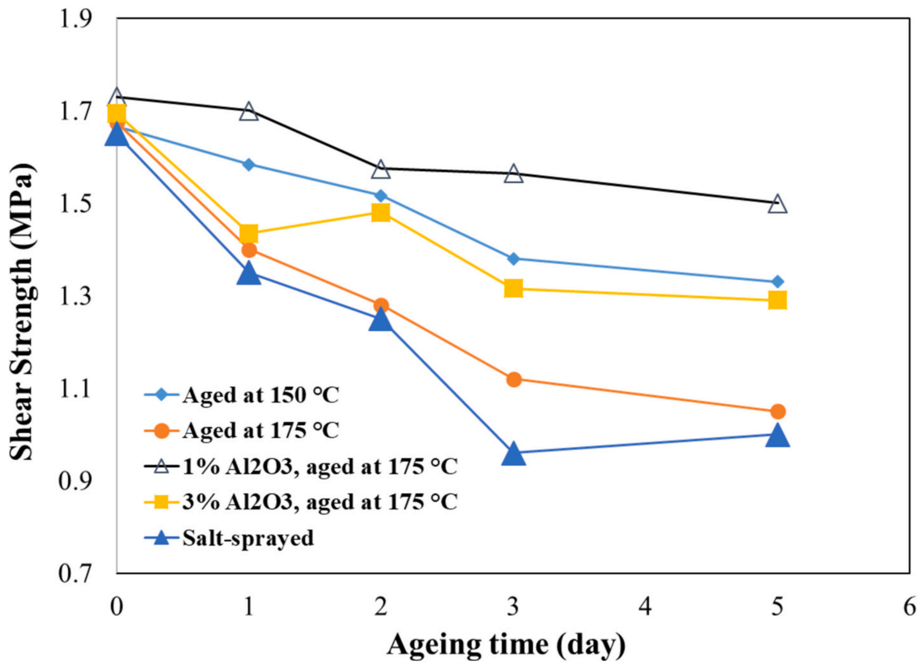

Fig. 6. Variation of shear strength for different ageing conditions.

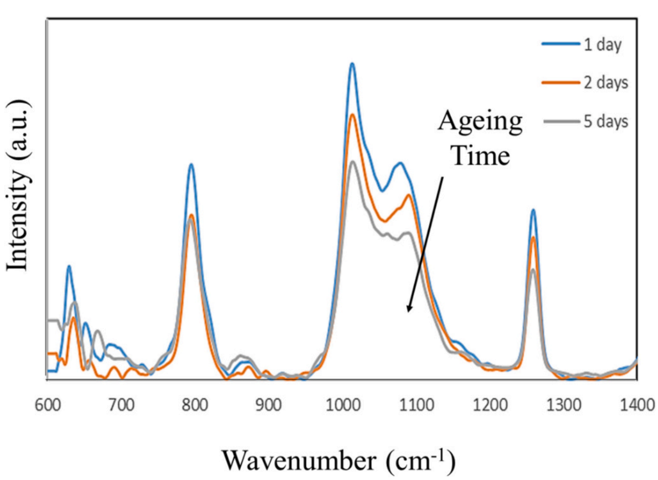

Fig. 7. FTIR of samples, aged for different time at 175 °C.

the mechanical properties of sealants.

CRediT authorship contribution statement

M. Yazdan Mehr: Conceptualization, Investigation, Writing – original draft. **P. Hajipour:** Methodology. **M.R. Karampoor:** Data curation, Methodology. **H. van Zeijl:** Validation, Supervision. **W.D. van Driel:** Supervision, Writing – review & editing. **T. Cooremans:** Validation, Writing – review & editing. **F. De Buyl:** Supervision, Writing – review & editing. **G.Q. Zhang:** Supervision.

Declaration of competing interest

We wish to confirm that there are no known conflicts of interest associated with this publication.

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Data availability

No data was used for the research described in the article.

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