International Journal of Adhesion & Adhesives 40 (2013) 103–107

Contents lists available at SciVerse ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Mechanical characterization of epoxy moulding compound in pressurized steam

M. Sadeghinia [a,*], K.M.B. Jansen [b], L.J. Ernst [a], H. Pape [c]

[a] Department of Precision and Microsystems Engineering, Delft University of Technology, Mekelweg 2, 2628 CD Delft, The Netherlands
[b] Department of Industrial Design Engineering, Delft University of Technology, Landbergstraat 15, 2628 CE Delft, The Netherlands
[c] Infineon Technologies AG, Germany

ARTICLE INFO

Article history:
Accepted 3 August 2012
Available online 21 August 2012

Keywords:
Epoxy
Creep
Viscoelasticity

ABSTRACT

Epoxy Molding Compounds (EMCs), commonly based on epoxy resin, are used widely for encapsulation of chips in electronic devices for protection against mechanical, environmental, and chemical attack. The thermo-mechanical properties of these compounds are important for the assessment of package reliability. These properties are highly dependent on the temperature and moisture.

EMCs absorb water when exposed to a humid environment. The trapped water generates steam in the compounds during the soldering reflow part of the packaging assembly process, which may drastically change the viscoelastic and adhesion behavior of the compound.

The present research focuses on the characterization of mechanical properties of an epoxy molding compound in steam at elevated pressure (temperature above 100 °C and relative humidity equal to 100%). A special steam chamber with a highly accurate tensile setup for force and displacement measurements is designed and manufactured. The chamber is equipped with a 3 Point Bending (3PB) loading setup. The setup can also be modified to mixed mode bending for investigating the effect of temperature and steam on the molding compound-to-lead frame interface strength.

In this paper, the viscoelastic creep compliance of a molding compound in dry and wet environment is measured in 3 point bending mode. It is shown that steam significantly affects the thermo-mechanical properties of the molding compound. The glassy and rubbery modulus of the molding compound were seen to decrease almost by 20%. Furthermore the glass transition temperature decreased by about 30 °C and the creep process was seen to be about a factor 40 faster in a hot steam environment.

1. Introduction

It is well known that polymers and polymer-based composites show strong temperature and time dependent behaviour. These viscoelastic properties are highly dependent on temperature, degree of cure and moisture. The first two factors have been reported in our previous works [1,2] while concerning the issues for epoxy molding compounds. In [1] the thermo-mechanical properties of a series of epoxy resins were studied. It was shown that the filler decreases the cure shrinkage and thermal contraction of epoxy resins. However it increases the modulus below and above the glass transition temperature. Moreover in [2], the changes in viscoelastic properties during cure for commercial molding compounds is monitored. Using a shear tool, a full cure dependent visco-elastic model for the shear modulus of these materials was extracted.

Studies showed that moisture in any form causes swelling and degradation in polymer composites. This factor can also (and generally does) affect the mechanical and physical properties of the polymers and composites, as described in many studies. [3–8] reported the moisture effect on the mechanical properties of a carbon/glass fiber hybrid composite, polyurethane shape memory polymer and EMCs and found out that the absorbed water continuously decreased the mechanical strength and T_g of the materials. Furthermore, Walter et al. and Boehme et al. [9–11] showed that the viscoelastic responses of the EMCs under dynamic loading are highly dependent on the temperature and moisture content of the samples. Similar phenomenon were also observed by Zhou et al., and Ishisaka and Kawagoe [12,13].

Epoxies are widely used in the microelectronic industries as encapsulants, adhesives and underfills. The mechanical properties of these materials and the interface strength of electronic chips are also affected by the generated steam during soldering reflow

---

[*] Corresponding author. Tel.: +31 152785707; fax: +31 152782150.
E-mail address: M.Sadeghinia@tudelft.nl (M. Sadeghinia).

0143-7496/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijadhadh.2012.08.006

of microelectronic assembly process. However, in studies where the moisture sensitivity of polymers was investigated the highest temperature was limited to the boiling point of water, 100 °C. Therefore, up to now, the thermo-mechanical properties of the molding compounds for the temperature/ humidity regime of temperature above 100 °C and relative humidity near 100% were not established.

The present research focuses on the viscoelastic properties of EMCs in steam at elevated pressure conditions. For the present harsh environment study a special steam chamber (Pressure Vessel) with a highly accurate tensile setup is designed and tested. The functionality and performance of the setup is assessed measuring the viscoelastic creep compliance of an EMC in dry condition and comparing that with creep measurements using a commercial Dynamic Mechanical Analyzer (DMA). Applying the time–temperature superposing principle, the viscoelastic creep compliance master curves and related shift factors are extracted and compared. As the next step, the mechanical properties of the EMC (creep compliance, T_g and corresponding shift factor) are determined for the pressurized steam environment and the effect of the moisture is quantified.

2. Design of the setup

A special steam chamber is developed in order to measure the viscoelastic properties of the EMC in pressurized steam. The simplified schematic diagram of this setup is shown in Fig. 1. The steam chamber with tensile setup initially contains 0.5 l water. This water converts to steam while heating up the setup. The initial air in the system is removed by a pressure release valve in top of the vessel (F in Fig. 1) such that the chamber always contains water vapor at 100% humidity. For temperatures above 100 °C this corresponds to a higher pressure, a relation which is known from standard thermodynamics [14].

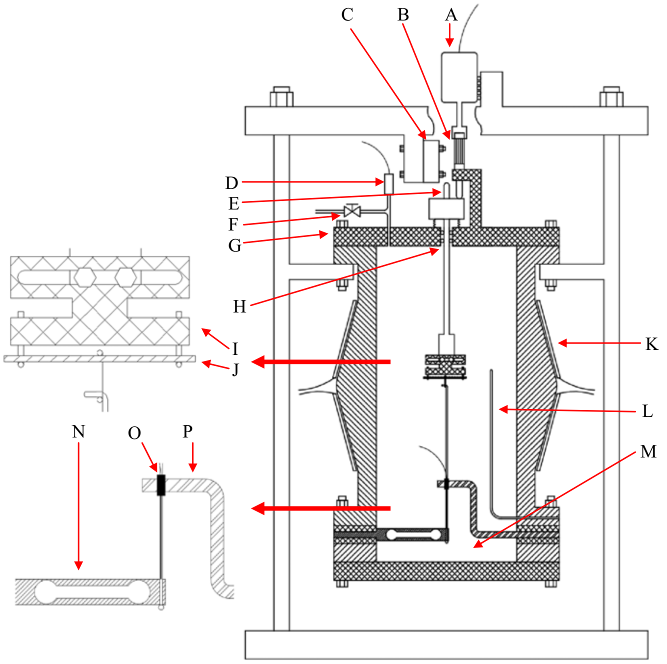

Fig. 1. Schematic drawing of pressure vessel apparatus (not to scale). A: programmable stepping motor with guiding fixture; B: controllable micrometer; C: displacement transducer (laser sensor); D: pressure transducer; E: shaft; F: pressure release valve; G: top flange; H: pressure seal; I and J: 3PB setup with sample; K: heating elements; L: thermocouple; M: water reservoir; N: force transducer (loadcell); O: Differential Variable Reluctance Transducer (DVRT); and P: DVRT holding fixture.

The designed and developed Pressure Vessel (PV) consists of a thick walled steel housing and a loading section. The loading section includes a 3 point bending set up (I and J), force transducer (N) and displacement measurement part. (B and C in Fig. 1)

The moving set up consists of a controllable micrometer (B), a step motor with holding fixture (A) and a shaft (E). The controllable micrometer is positioned on top (=outside) of the vessel in the relatively cool area and is driven by a programmable stepping motor. The movable shaft enters the upper flange plate through a hole with appropriate pressure seal. The upper side of the shaft is clamped by the guiding fixture, moving the shaft vertically. The movement of the shaft is captured by the displacement transducer (Laser sensor, 2820 KEYENCE Co.) mounted outside of the vessel.

As Fig. 1 shows the 3PB setup along with the sample are positioned at the lower part of the movable shaft. The 3PB setup can be used for specimen with various dimensions. It is also possible to replace it with a mixed mode bending setup for doing delamination measurements [15,16].

A rigid rod connects the sample to the load cell positioned on the lower flange plate inside the vessel. The load cell consists of a hollow beam (N) of which the deflection is measured using a Differential Variable Reluctance Transducer (O in Fig. 1, type: M-DVRT-1.5 mm, high resolution, Microstrain Co.). This DVRT is especially chosen for this application as it can operate at temperatures up to 170 °C in humid environments, while strain gauges are unreliable under these extreme conditions.

For a 3PB experiment the sample is loaded by moving the shaft upwards. The applied load and displacement of the load cell are monitored by recording the voltage differences of the DVRT. These voltages are converted to load and displacement of the DVRT using a calibration curve. The calibration data is obtained by applying known loads and displacement to the load cell at different temperatures, ranging from 100 to 180 °C. The force and displacement calibration factors turn out to be 1.13 N/V and 0.406 mm/V and are slightly temperature depended. Calibration factors in wet conditions are much more involved and were performed at only two temperatures (120 °C and 135 °C) which agreed well with dry condition.

The load cell is designed for relatively low forces (up to 2 N). Therefore the beam of the load cell has a non-negligible displacement which must be considered. The displacement of the sample is defined as the difference between the shaft and loadcell displacement.

The chamber of the pressure vessel includes three parts: top, middle and lower. The lower section contains the water reservoir and is made from a bolted flange with flange plate. This section also comprises the loadcell and DVRT. The middle section has two removable glass windows for sample mounting and observation. Condensation of steam on the glass windows is effectively prevented by a thin coating (Rain-x, Anti- rain, Shell Car Care International Ltd.) and by external heating of the windows using a hot air blower. Furthermore, this section is equipped with heating elements (6000 W, WATLOW Co.) and thermocouple (K and L in Fig. 1). The top part is made up from a bolted flange with flange plate on which the motion part with laser sensor is installed. This section also entails the pressure transducer (0–10 bar, WIKA Co.) measuring the inside steam pressure. All signals are analyzed using a dedicated Lab View program.

3. Experiments

3.1. Material

A commercial epoxy molding compound (MP8000, Nitto Co.) was molded into strips of 38 × 5 × 2 mm^3 by NXP Semiconductor

Co., Nijmegen. It contains about 75% silica filler particles and has a glass transition temperature of about 160 °C, measured by DMA technique. The material was selected such that it remains in its viscoelastic range under the pressurized steam conditions, studied here.

3.2. Mechanical properties in dry environment

As a start, the newly constructed apparatus was tested by doing creep measurement in dry condition. The extracted mechanical properties are then compared to the creep data obtained from a commercially available apparatus (Dynamic Mechanical Analyzer, DMA Q800, TA Instruments Co.) in 3 point bending mode with the same sample size of $20 \times 2 \times 0.5$ mm^3. The experiments cover the temperature range of 100–190 °C. The compliances vs. time graphs of both measurements are plotted in Figs. 2 and 3.

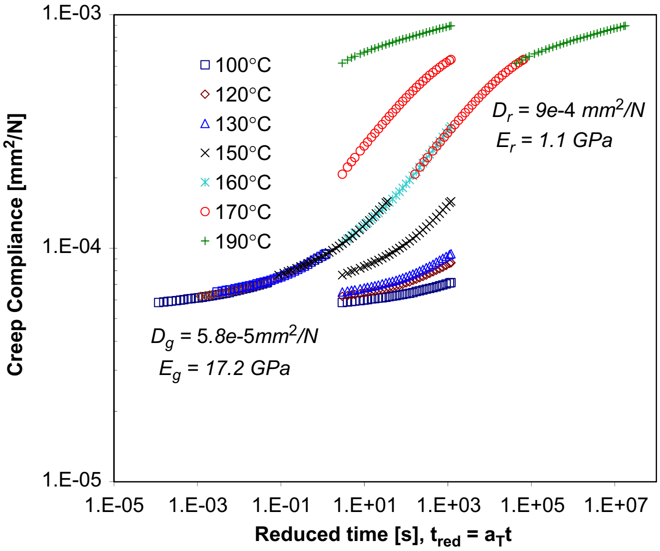

Fig. 2. DMA measurement of the 3PB creep compliance of the EMC sample along with the corresponding master curve at dry environment. Symbols: measured data in different temperatures. T_{ref}=160 °C.

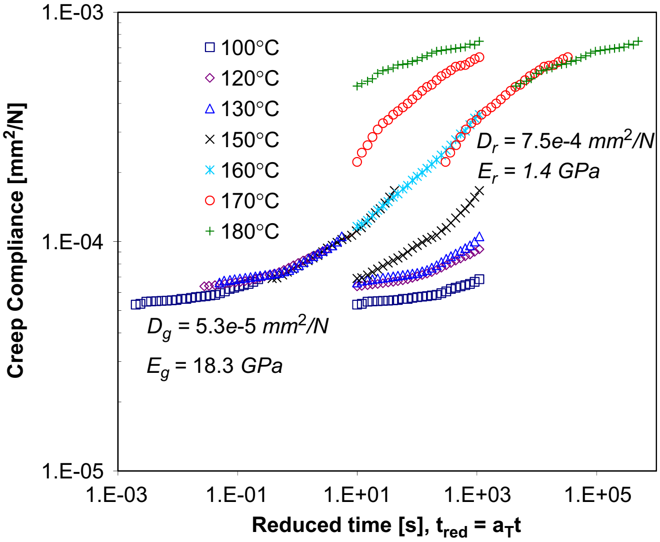

Fig. 3. Pressure vessel measurement of the 3PB creep compliance of the EMC sample along with the corresponding master curve at dry environment. Symbols: measured data at different temperatures. T_{ref}=160 °C.

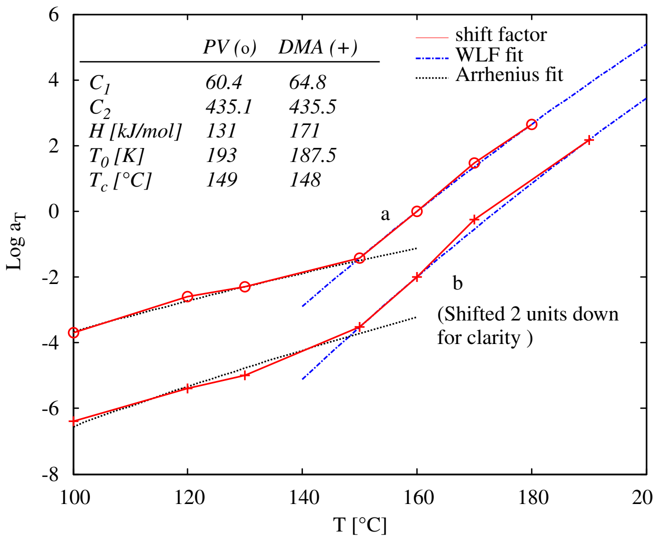

Fig. 4. Full line: shift factors corresponding to the master curves of Figs. 2 and 3, dash lines: WLF and Arrhenius model along with fitting parameter. Symbols: measurement data, T_{ref}=160 °C. Curve a and b refer to the pressure vessel and DMA results, respectively.

Time–temperature superposition [17] was applied for both sets of measurements. The creep compliance master curves were constructed by horizontal shifting of the compliance curves on the logarithmic time scale by a shift factor a_T, using T=160 °C as the reference temperature. This temperature was selected such that the material is in the middle of its viscoelastic range. The reduced time is defined as the creep time multiplied by a shift factor a_T, i.e. $t_{red}=a_T t$. The respective values for the shift functions are shown in Fig. 4. At higher temperatures the curves could be fitted to the so-called WLF-equation, Eq. (1) [18], whereas below the so-called switching temperature T_c an Arrhenius model was used, Eq. (2) [19]. The extracted fitting parameters are shown in Fig. 4.

$$\log a_T^{WLF} = \frac{C_1(T-T_{ref})}{C_2+T-T_{ref}} \qquad T \geq T_c \tag{1}$$

$$\log a_T^{Arrh} = \frac{-H}{2.30R}\left(\frac{1}{T}-\frac{1}{T_0}\right) \qquad T \leq T_c \tag{2}$$

where H and R denote the activation energy and gas constant respectively. C_1, C_2, and T_0 are the fitting parameters.

As Figs. 2 and 3 show there is a relatively small difference in glassy and rubbery elastic modulus values. In the viscoelastic region the compliance continuously increased. The obtained master curves appear to be almost identical in the viscoelastic region. The deviation in the glassy and rubbery regions are 1.1 and 0.3 GPa respectively which are relatively small and can be considered as the measurement errors.

Due to the compliance deviation in the glassy state, small differences in the corresponding shift factors are also observed. However above the switching temperature, the shift factor curves are almost identical (Fig. 4).

A separate independent heating scan (not shown) was performed on the DMA at 1 Hz on an EMC sample (size of $22.6 \times 2 \times 0.5$ mm^3) to have a better access to the glassy and rubbery plateaus values and to establish the glass transition temperature. This resulted in an elongation glassy modulus of 18 GPa and a rubbery modulus of 1 GPa. The T_g was determined as 162 °C based on the temperature at which E_g reduced by a factor 3.

3.3. Creep under high pressure steam condition

The viscoelastic creep compliance of the EMC in wet condition was measured using the 3PB set up in the pressure vessel. The sample is placed in the setup and connected to the load cell via the lower shaft. The glass window is closed and securely tightened. The temperature of the test section (and water/steam mixture) is set to the required value.

During the heating up procedure the air/steam mixture was vented through a pressure release valve in top of the vessel. After some hold time at the set temperature the remaining air is negligible and the release valve is closed. It takes about 1 h to reach the required temperature with steam inside the chamber. Afterwards, a hold time of 3 h is programmed for the moisture to diffuse in the EMC. Above 100 °C the estimated coefficient of moisture diffusion for these materials are about 10^{-11} m^2/s [8]. Therefore, for a sample thickness of 0.5 mm a saturation of 95% is reached after 1.3 h.

The measured creep compliances are plotted in Fig. 5. Applying the time–temperature superposition principle, the related master curve and shift factors are also extracted assuming T_{ref}=120 °C, Fig. 5 and 6. 120 °C was selected as the reference temperature since the material is in the middle of its glass transition region.

It is known that the process of moisture absorption in polymers is accompanied by swelling which is always associated with changes in the mechanical properties.

As Fig. 6 shows the absorbed water decreases the glassy and rubbery elastic moduli by almost 20%. In addition water absorption speeded up the relaxation process. Similar phenomena were observed in previous studies [7–13]. The shapes of the master curves seem to be almost identical in both environments. However the creep occurred almost 40 times faster in moisturized condition and the master curve transferred to the shorter time scale. This phenomenon can be attributed to the T_g decrease in wet status.

The T_g in creep measurement can be estimated assuming a cross plot of creep compliance vs. temperature at 100 s (based on Figs. 3 and 5). The extracted compliances are plotted in Fig. 7. The glass transition temperature for creep measurements ($T_g^{creep,100s}$) is defined as the temperature with the threshold compliance of the glassy compliance increased by the factor 3. The obtained

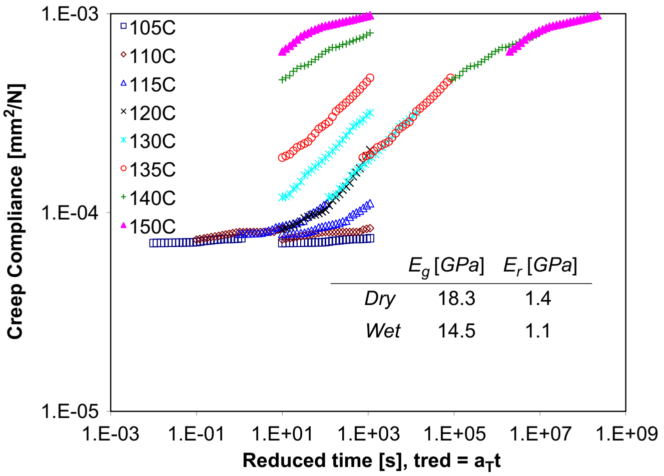

Fig. 5. EMC elongation creep compliance in wet environment and master curve obtained after time–temperature superposition, T_{ref}=120 °C.

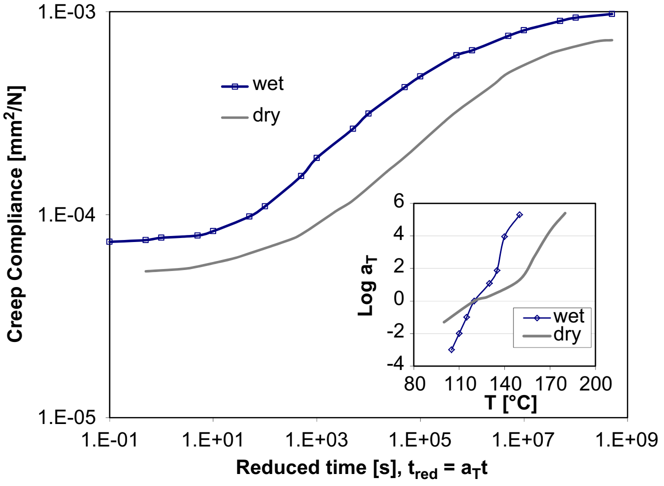

Fig. 6. Creep compliance master curve in dry and wet environment along with the corresponding shift factor, T_{ref}=120 °C.

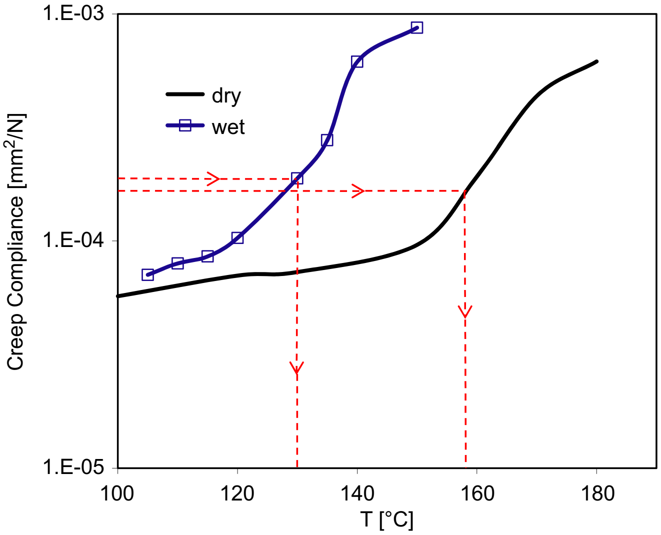

Fig. 7. Pressure vessel measurments for the creep compliance vs. temperature. Datas are extracted from the cross plot of creep compliance vs. temperature at 100 s, based on Figs. 3 and 5.

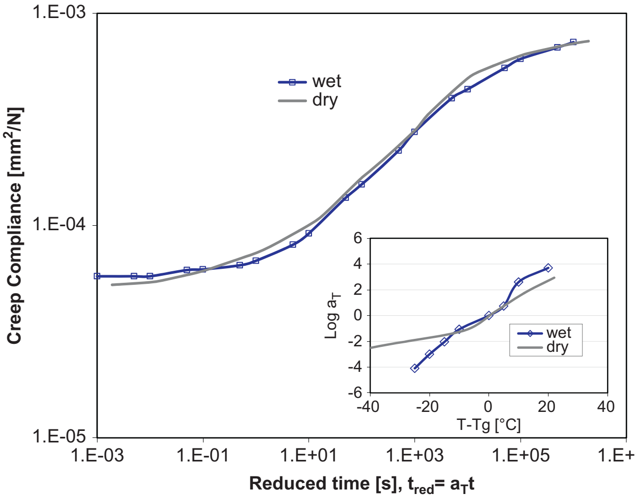

Fig. 8. Creep compliance master curves for $T_{ref}=T_g^{creep,100\,s}$ along with the shift factor. Full lines: dry, line with symbols: wet.

values for T_g are then 158 °C and 130 °C for dry and wet condition, respectively. The dry value is close to that obtained from the DMA measurement (162 °C, Section 3.2).

The creep compliance master curves are reproduced assuming the $T_g^{creep,100s}$ as the reference temperature. Firstly, the wet measured compliance data moved with a constant vertically shift factor of 0.82. Afterwards the time–temperature superposition principle are applied for the dry and wet data and the new master curves are extracted using $T_{ref}=T_g^{creep,\ 100s}$. Fig. 8 illustrates that now the master curves overlap each other very well.

For each of the compliance master curves in Fig. 8 there is a corresponding temperature-shift factor graph. If the shift factors are plotted vs. $T–T_g$, it turns out that the horizontal shift factor values are similar in the viscoelastic temperature range ($T–T_g$ of −15 °C to 5 °C) but deviate in both the rubbery and glassy range.

4. Conclusions

In this study the thermo-mechanical properties of an Epoxy molding compound in harsh environment is investigated. A special steam chamber with a highly accurate tensile setup is designed. The performance of the set up in dry condition is verified measuring the creep compliance of the EMC sample. Furthermore, the viscoelastic creep compliance of the EMC in wet environment was extracted and it was observed that steam considerably changes the EMC's mechanical properties. Moisture decreased the elastic glassy and rubbery modulus by almost 20%. In addition the glass transition temperature is decreased by almost 30 °C.

Applying the time–temperature superposition principle, the master curves were extracted for dry and wet environment and it is shown that moisture shifts the compliance master curve to the shorter time domain. The dry and wet master curves coincide if the actual T_g is taken as the reference temperature.

Acknowledgments

Authors appreciate the European Commission for funding this work in FP7 under project NanoInterface (NMP3-SL-2008-214371). We acknowledge lab staff of TUDelft, Mr. H.F.L. Jansen, P. van Holst, R. Luttjeboer and J.A.S van Driel. Authors also thank Amar Mavinkurve from NXP semiconductor Co. for preparing the molding compound samples.

References

[1] Sadeghinia M, Jansen KMB, Ernst LJ. Characterization and modelling the thermo-mechanical cure-dependent properties of epoxy molding compound. Int J Adhes Adhes 2012;32:82–8.
[2] Sadeghinia M, Jansen KMB, Ernst LJ. Characterization of the viscoelastic properties of an epoxy molding compound during cure. J Microelectron Reliab 2012;52:1711–8.
[3] Tsai YI, Bosze EJ, Barjasteh E, Nutt SR. Influence of hygrothermal environment on thermal and mechanical properties of carbon fiber/fiberglass hybrid composites. J Comp Sci Tech 2009;69:432–7.
[4] Yang B, Huang WM, Li C, Chor JH. Effects of moisture on the glass transition temperature of polyurethane shape memory polymer filled with nano-carbon powder. Eur Polym J 2005;41:1123–8.
[5] Yang B, Huang WM, Li C, Li L. Effects of moisture on the thermomechanical properties of a polyurethane shape memory polymer. J Polym 2006;47:1348–56.
[6] Lu MG, Shim MJ, Kim SW. Effects of moisture on properties of epoxy molding compounds. J Appl Polym Sci 2001;81:2253–9.
[7] Ma X, Jansen KMB, Ernst LJ. Moisture effects on the creep of thermosetting IC packaging polymers. In: Proceedings of 7th EuroSime conference. Como; 2006. pp. 1–5.
[8] de Vreugd Y. The effect of aging on moulding compound properties. PhD thesis. Delft University of Technology, Delft; 2011.
[9] Walter H, Dermitzaki E, Shirangi H, Wunderle B, Hartmann S, Michel B. Influence of moisture on the time and temperature dependent properties of polymer systems. In: Proceedings of 10th EuroSime Conference. Delft; 2009. pp. 1–5.
[10] Walter H, Dermitzaki E, Wunderle B, Michel B. Influence of moisture on humidity sensitive material parameters of polymers used in microelectronic applications. In: Proceedings of 3rd ESTC conference. Berlin; 2010. pp. 1–5.
[11] Boehme B, Roellig M, Wolter KJ. Measurement of viscoelastic material properties of adhesives for shm sensors under harsh environmental conditions. In: Proceedings of 11th EuroSime conference. Bordeaux; 2010. pp. 1–10.
[12] Zhou SM, Tashiro K, Ii T. Confirmation of universality of time–humidity superposition principle for various water-absorbable polymers through dynamic viscoelastic measurements under controlled conditions of relative humidity and temperature. J Polym Sci B: Polym Phys 2001;39:1638–50.
[13] Ishisaka A, Kawagoe M. Examination of the time–water content superposition on the dynamic viscoelasticity of moistened polyamide 6 and epoxy. J Appl Polym Sci 2004;93:560–7.
[14] Doty S, Turner WC. Energy management handbook. 7th ed. Lilburn, GA: Fairmont Press; 2009.
[15] Reeder JR, Crews JR. Mixed mode bending method for delamination testing. J. AIAA 1990;28(No.7):1270–6.
[16] ASTM D 6671-01. Standard Test Method for Mixed Mode I–II interlaminar fracture toughness of unidirectional fiber reinforced polymer matrix composites. Annual book of ASTM standards, vol. 15.03. American Society for Testing and Materials. West Conshohocken, PA; 2001.
[17] Ferry JD. Viscoelastic properties of polymers. 3rd ed. New York: Wiley; 1980.
[18] Williams ML, Landel RF, Ferry JD. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. J Am Chem Soc 1955;77:3701–7.
[19] McNaught AD, Wilkinson A. Compendium of chemical terminology. 2nd ed. Oxford: IUPAC Blackwell Scientific; 1997.