Effect of filler concentration of rubbery shear and bulk modulus of molding compounds

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Abstract

In the electronics industry epoxy molding compounds, underfills and adhesives are used for the packaging of electronic components. These materials are applied in liquid form, cured at elevated temperatures and then cooled down to room temperature. During these processing steps residual stresses are built up resulting from both cure and thermal shrinkage. In order to minimize these stresses inorganic fillers are added. These fillers have several opposing effects on the residual stresses because they decrease the cure shrinkage and thermal contraction but increase the modulus below and above the glass transition temperature. In this paper an extensive study on the cure-dependent rubbery moduli of a series of silica spheres filled epoxy resins is carried out both experimentally and theoretically. Low frequency dynamic mechanical analysis (DMA) was used to measure the rubbery modulus build-up during cure. A model based on scaling analysis was applied to describe the evolution of the rubbery shear modulus. The effect of the filler percentage on the rubbery shear and bulk moduli as well as the coefficients of thermal expansion were measured and compared with models from the theory of particulate-filled composites.

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1. Introduction

Thermosetting polymers are widely used in the electronics industries as encapsulants, adhesives and underfills, etc. It is well known that polymers and polymer-based composites show strong temperature and time dependent behavior, i.e. viscoelastic behavior. Stress relaxation under constant deformation and creep under constant stress level are the main characteristics. Fig. 1 illustrates this schematically. At temperatures well below the glass transition temperature $T_g$, polymers exhibit a relatively high modulus, called the glassy modulus. As the temperature is increased through $T_g$, the material goes through the transition region and the stiffness drops dramatically to a value called rubbery modulus or equilibrium modulus. For un-crosslinked polymers, such as thermoplastics, the stiffness exhibits only a very short plateau and then decrease to zero and the material behaves like a viscous liquid. For crosslinked polymers, the amplitude of the rubbery plateau depends on the crosslinking density. The rubbery moduli dominate the material response at high temperature or at long times. The curing step (hardening or crosslinking of the molding compound) is a critical step for IC packaging. During the curing step the thermosetting polymer gradually transforms from the liquid state into a viscoelastic solid with a relatively high glassy modulus. Before the gel point, the rubbery shear modulus is zero and it increases as the curing proceeds. Cure-induced stresses will arise in areas where shrinkage is prevented by geometrical constraints. Although part of the residual stress will relax because of the material’s viscoelastic behavior, there is a certain amount of the residual stress which is dependent on the...
rubbery moduli and will not relax to zero within the service time. This part will not relax even at elevated temperature or long time. The rubbery moduli determine part of the cure-induced stresses.

The residual stresses after encapsulation roughly consist of three parts: cure shrinkage stresses, stresses due to cooling above \( T_g \) and stresses due to cooling below \( T_g \). The first two contributions are proportional the rubbery modulus whereas the last contribution depends on the glassy modulus. A first estimate of the relative importance of these contributions can be obtained by assuming the modulus to change stepwise at the glass transition from its rubbery value \( G_r \) to its glassy value \( G_g \). In that case the contributions will be proportional to \( G_r \Delta \varepsilon_{\text{cure}} \), \( G_r \Delta \varepsilon_{\text{rubbery}}(T_c - T_g) \) and \( G_g \Delta \varepsilon_{\text{glassy}}(T_g - T_{\infty}) \) respectively (here \( \Delta \varepsilon \) denotes the thermal expansion mismatch between compound and substrate or chip). Usually the last contribution (cooling down below \( T_g \)) dominates but the relative importance is highly dependent on details of the experimental parameters. In this paper we focus on the filler effects. With the above estimates it can be seen that a higher filler concentration has several opposing effects on the amount of residual stresses. First of all, an increase in filler loading increases both the glassy and rubbery moduli such that all three contributions increase. The second effect is that both the rubbery and glassy CTEs decrease, resulting in a decrease in CTE mismatches and thus a decrease of (mainly) the second contribution. The third effect is that the cure shrinkage decreases linearly with the volumetric filler fraction. Therefore, it is vital to accurately measure and model the evolution of the rubbery moduli.

Studies on the rubbery properties and cure models of polymers have been reported, for example, in [1–4]. In [1], a rubbery elastic shrinkage model was proposed for predicting cure stresses in Epon 828/EDA resin. In [2], an investigation on the residual stress build-up in thermoset films cured above their \( T_g \) was conducted and it was indicated that the residual stress level induced in curing above \( T_g \) depends much on the materials. A model based on scaling analysis was proposed for modeling the evolution of rubbery shear modulus during cure [3]. The theory of rubber elasticity was also used to model temperature and conversion dependent equilibrium shear modulus of an epoxy resin [4]. In [5,6], a micromechanics approach was used to predict the modulus of underfill materials. Such approach was also used for analysis of the thermoelastic behavior of filled molding compound [7]. Most of the previous studies have been on the elastic properties.

In this paper, we will investigate which models are suitable to describe the effect of filler concentration on both the rubber shear and bulk modulus as well as on the coefficient of thermal expansion. The experimental work was carried out on a series of home made Epoxy Molding Compounds. In Section 2, the experimental methods for measuring the evolution of the rubbery moduli are described. In Section 3 we discuss the effect of filler on the thermal expansion whereas in Section 4 the evolution of the rubbery shear modulus is studied. Finally, in Section 5, several models from the theory of particulate-filled composites were used to calculate the rubbery moduli of molding compounds with different filler loadings.

2. Experimental

2.1. Materials and sample preparation

The material used for this study is a particulate-filled composite containing similar components as used in commercial molding compounds. The system consists of epoxy Novolac (EPN 1180, Huntsman Advanced Materials, equivalent weight 175–182 g/eq) as a matrix material, Bisphenol-A (equivalent weight 114 g/eq) as hardener and fused silica spheres (FB-940, ex Denka, median diameter 15 μm, density 2.20 g/cm³) as filler. Triphenylphosphine (TPP, 0.5 g/100 g epoxy) is used as a catalyst. The epoxy Novolac and Bisphenol-A were mixed in a stoichiometric ratio. The materials with applied filler loadings of 0, 40, 50 and 65 wt% (25, 33 and 50 vol.%) will be denoted as F00, F40, F50 and F65.

2.2. Thermal expansion measurements

The coefficients of thermal expansion were measured in a TA-Instruments TMA 2940 by Philips Semiconductors. The applied heating rate and force were 10 °C/min and 1 N, respectively. The CTE values were determined from the second heat scans.

2.3. Low frequency DMA

For fully cured material, DMA, relaxation and creep tests can be used to measure the rubbery modulus. The tests should be conducted at a temperature well above the ultimate \( T_g \). It is much more difficult to measure the rubbery modulus during the curing process. In that case relaxation and creep tests are not suitable due to the ongoing stiffness build-up as the curing proceeds. Therefore a novel method called ultra low frequency scan (ULFS) DMA was used to characterize the rubbery modulus during cure. In this method a displacement oscillation with a
very low frequency (e.g. 0.001–0.01 Hz) is applied to the sample during isothermal cure at a temperature above the glass transition, $T_g$ and the reacting force is measured. The rubbery modulus is directly proportional to the force amplitude and is seen to rise gradually as cure proceeds. Preliminary tests at both 0.005 and 0.01 Hz showed that measured modulus values for these epoxy systems were frequency independent, which shows that we really measure the rubbery plateau values. Fig. 2 shows schematically the low frequency DMA method for the rubbery measurement. Displacement oscillation with constant amplitude was applied to specimen and reacting force was recorded. As the curing conversion increases, passing through the gel point, the amplitude of the force increases. The rubbery modulus can be calculated either using the force amplitude within one cycle or using the increment of the displacement and force during a certain time increment.

The DMA tests during cure were performed in a Metra-vib VA4000 viscoanalyzer using a dual plane shear test setup as shown schematically in Fig. 3. Displacement is applied by the moving part and the base plate is connected to the force transducer. The measured stiffness, storage modulus and the loss modulus can be output and analysed through the program with test machine. The force and displacement signals were recorded simultaneously through the output ports by a data acquisition system for subsequent analysis as discussed above.

### 2.4. Bulk modulus measurement setup

The rubbery bulk modulus was measured using a disc-specimen test clamped between two rigid plates (poker-chip test, Fig. 4). Close to plate surfaces the radial displacements are prevented and if the specimen thickness is small compared to its diameter the specimen will be in a unilaterial compression state. In this state both the shear modulus $G$ and the bulk modulus $K$ contribute. Lindsey et al. [11] derived an approximate solution by assuming a uniform stress through the specimen thickness. The axial stress component is given by Eq. (1) as:

$$
\sigma_z = \frac{\varepsilon}{3} \left\{ (3K - G) + (5G - 3K) \cdot \frac{I_0(3a\sqrt{\frac{G}{3K + G}})}{I_0(3a\sqrt{\frac{G}{3K + G}})} \right\},
$$

where $a$ is the outer radius of the specimen, $r$ the distance from the center and $I_0$ the modified Bessel function. The axial stiffness $M_z$ is given by:

$$
M_z = \frac{\int_0^a \sigma_z \pi r^2 \text{d}r}{\varepsilon}
$$

Fig. 5 shows the experimental setup for measuring the rubbery bulk modulus. The two aluminum plates with a diameter of 50 mm are installed in a Zwick 1474 testing machine. The upper plate is fixed and connected to the force transducer. The lower one is connected to the crosshead of the testing machine and the axial displacement is controlled by an LVDT (linear variable displacement transducer). The plates were heated above the ultimate $T_g$ of the resin. The thickness of the specimen is about 2 mm. Liquid resin was injected between the plates and cured. Low frequency axial oscillations (displacement
controlled mode) were applied to the fully cured specimen and the reacted axial force was recorded. The bulk modulus was calculated through Eqs. (1) and (2).

3. Filler loading effects on coefficient of thermal expansion

The coefficient of thermal expansion (CTE) for the fully cured molding compounds with different filler concentrations are shown in Fig. 6. As expected both the glassy and rubbery CTEs decrease with filler loading. The values of the rubbery CTE are approximately a factor 3 larger than those in the glassy state, which is an observation that holds for most polymers.

As a first approximation we can assume that the total expansion is just the sum of the expansion of the polymer matrix and that of the filler particles (rule of mixtures):

$$
\beta_{CTE} = \beta_{CTE, f} \phi_f + (1 - \phi_f) \beta_{CTE, m}
$$

where \( \phi_f \) is the vol.% of filler which is related to the wt% of filler, \( \phi_f \) through

$$
\phi_f = \frac{\rho_f \phi_f}{\rho_f \phi_f + \rho_m (1 - \phi_f)}
$$

in which \( \rho_f \) and \( \rho_m \) denote the density of the filler particles and the unfilled matrix (being 2.20 and 1.16 g/cm\(^3\), respectively). \( \beta_{CTE, f} \) and \( \beta_{CTE, m} \) stand for the volumetric CTEs of the filler and matrix materials, respectively. The CTE of the silica filler is taken as \( 4 \times 10^{-7} \) K\(^{-1}\). Fig. 6 clearly shows that Eqs. (3) and (4) are in fact a very good approximation for the actually observed CTEs, certainly regarding the fact that the model does not contain fit parameters. Only the rubbery CTEs for the 40 and 50 wt% samples are larger than the rule of mixture predictions. These differences are probably caused by small air gaps at the filler interfaces resulting in a non negligible extra expansion.

4. Conversion dependency of rubbery shear modulus (ULFS method)

The results of the ultra low frequency scan method and the applied temperature profile are shown in Fig. 7. The resin was cured in two steps: first at 130 °C for 5 h and the at 160 °C for 2 h. Afterwards, the sample was cooled step wise down to 120 °C to check the temperature dependency of the fully cured rubbery modulus. The frequency used is 0.01 Hz. It can be seen that the modulus is zero at liquid state and increases from certain point (the gel point). It also shows a slight increase with increasing temperature. Below 125 °C, the frequency is not suitable for the rubbery modulus measurement. e 50% filled material.

Fig. 8 shows the modulus build-up with conversion level for all materials at 130 °C. It can be seen that before 80% conversion, the modulus is very low. After that, it increases quickly during the final conversion period. Nearly two third of the modulus is built up in the conversion range from 90% to 100%. It also indicates that the filler percentage has significant reinforcement on the rubbery modulus, especially at highly filled state. The 65% filled compound (denoted as F65) shows a sharp increase of rubbery modulus compared to the 50% filled material.

Based on scaling analysis, Adolf and Chambers [3] proposed a model to describe the evolution of the equilibrium shear modulus:

$$
G_r(\tilde{x}, T) = G_r^0(T) \left[ \frac{\tilde{x}^2 - \tilde{x}_{gel}^2}{1 - \tilde{x}_{gel}^2} \right]^{8/3}
$$

where \( \tilde{x} \) is the degree of conversion and \( \tilde{x}_{gel} \) is the conversion the gel point. \( G_r^0(T) \) is the rubbery shear modulus at
the fully cured state \((\alpha = 1.0)\), which is considered temperature dependent.

Figs. 9 and 10 show a comparison of the experimental measurement and the model prediction of the rubbery shear modulus for the materials with different filler loading during 130 °C isothermal cure. The solid lines in the figures represent the prediction of (Eq. (5)), which turns out to agree well with the experimental data. The evolution of the conversion level with curing time was calculated from Kamal and Sourour’s kinetic model. For details see references [9] and [10].

In order to model the cure dependency of the rubbery bulk modulus, we propose an equation similar to that of Eq. (5):

\[
K_r(\alpha, T) = K^l_r + \left[K^l_r(T) - K^l_f\right] \left[\alpha^2 - \alpha^2_{gel}\right]^{8/3},
\]

in which \(K^l_r\) is the bulk modulus at the liquid state, \(K^l_f\) is the bulk modulus at the fully cured state. The extra constant \(K^l_f\) in Eq. (6) is added to ensure a minimum value for the bulk modulus. A zero value for the bulk modulus would have been unacceptable from a physical point of view since this corresponds to a material with zero resistance to hydrostatic compression. The bulk modulus of liquid molding compounds is expected to be close to that of other liquids, i.e. in the range from 1 to 3 GPa.

5. Modeling of filler loading effects on rubbery shear and bulk modulus

The particulate filled molding compound can be considered as a two-phase composite consisting of an isotropic viscoelastic matrix and randomly distributed isotropic elastic particles. In rubbery state, the rubbery elastic property of the resin is dominant. Therefore, micromechanics approach can be used for predicting the properties of the composites.

5.1. Mori–Tanaka method

According to Mori–Tanaka theorem [12], the effective shear and bulk modulus of the composites is given by:

\[
G_e = G_m \left\{ \frac{1 + \phi_f (G_t - G_m)}{G_m + 2\phi_m (1 - \phi_f)(G_t - G_m)} \right\}
\]

\[
K_e = K_m \left\{ \frac{1 + \phi_f (K_t - K_m)}{K_m + 3\gamma_m (1 - \phi_f)(K_t - K_m)} \right\}
\]

where

\[
\gamma_m = \frac{1 + \nu_m}{9(1 - \nu_m)}
\]

\[
\delta_m = \frac{4 - 5\nu_m}{15(1 - \nu_m)}
\]

in which, \(G\) and \(K\) are the shear and bulk modulus, \(\nu\) is the Poisson’s ratio and \(\phi_f\) is the volume fraction of the filler (Eq. (4)). Subscript \(m\), \(f\) and \(c\) refer to the matrix, filler and composite material, respectively.

5.2. Differential effective medium theory

In the differential scheme, it is assumed that the filler is added gradually to the composite, starting with pure matrix. The changes of macroscopic properties of the composite due to an infinitesimal increase of particle concentration are given in differential (incremental) forms. Thus the composite with particle volume fraction \(\phi_t\) is regarded as a homogenous effective medium with equivalent macroscopic properties. When an infinitesimal amount of particles (with volume fraction increment \(d\phi_t\)) is added to the composite, the change of the composites properties is given by:

\[
dG = gG \frac{1}{1 - \phi_t} \ d\phi_t
\]

\[
dK = kK \frac{1}{1 - \phi_t} \ d\phi_t
\]

in which \(g\) and \(k\) depend on \(G\) and \(K\) for the matrix at the given value of \(\phi_t\). For spherical particles, the values of \(g\) and \(k\) are:

\[
g = \frac{5(K + \frac{4}{3}G)(G_t - G)}{3G(K + \frac{8}{3}G) + 2G_t(K + 2G)}
\]

\[
k = \frac{(K + \frac{4}{3}G)(K_t - K)}{K(K_t + \frac{4}{3}G)}
\]
By integrating these coupled equations, the effective properties can be obtained.

5.3. Eilers equation

Eilers equation was based on the relationship between the relative viscosity and the volume fraction of the disperse phase [13] and is often used to describe the effect of filler on the rubbery modulus. The Eilers expression for the rubbery shear modulus of the composite is:

\[ G_c = G_m \left(1 + \frac{1.25 \phi_f}{1 - \phi_f/\phi_m}\right)^2 \]

where \( \phi_m \) is the maximum packing fraction for the filler. Because the sizes of the used silica spheres range from a few microns to about 50 \( \mu m \), a higher \( \phi_m \) is expected than would be possible for a compound with uniform filler size. In this paper \( \phi_m = 0.78 \) is used.

5.4. Results and discussion

Fig. 11 shows the experimental rubbery shear modulus of the fully cured materials with different filler volume fraction (symbols). It can be seen that the predictions from three models all agree well at relatively low filler concentra-

\[ G_c = G_m \left(1 + \frac{1.25 \phi_f}{1 - \phi_f/\phi_m}\right)^2 \]

tions (<30% by volume). At high filler concentration, the Eilers equation gives a better prediction and the Mori–Tanaka method and Differential Scheme clearly underestimate the modulus values.

The rubbery bulk modulus versus filler volume fraction is shown in Fig. 12. The results indicate that the predictions of both the Mori–Tanaka and the Differential Scheme model agree well at relatively low filler concentration but underestimate the bulk modulus considerably at the highest filler concentration. The Eilers model is not used here since it is only suitable for shear modulus predictions.

6. Conclusions

In this paper, an investigation with focus on the effect of the filler loading on the rubbery shear and bulk moduli of a series of epoxy resins is carried out both experimentally and theoretically. With a new ultra low frequency DMA method it turned out to be possible to measure the rubbery modulus build-up during cure. The resulting experimental data showed that most of the modulus built-up occurred during the last 10% of conversion. The increase of the rubbery modulus was well captured with Adolf’s model [3]. The variation of fully cured rubbery shear modulus with filler loading turned out to be best described with the Eilers model, whereas for the effect of filler on the rubbery bulk modulus the differential scheme method is preferred. The variation of the coefficient of thermal expansion with filler concentration is conveniently modelled with a simple rule of mixtures.

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