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Time–temperature transformation (TTT) cure diagram of a fast cure non-conductive adhesive

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Abstract

The conductivity of a non-conductive adhesive (NCA) interconnect is completely dependent on the direct mechanical contact between the IC bump and the substrate pad. According to our previous research, the evolution of the cure shrinkage, cure stress and even the interfacial adhesion strength are highly related to the curing process and the phase transformation of NCA. Therefore, a good understanding of curing process which involves time–temperature transformation (TTT) is of great importance for providing an optimal cure schedule. In this paper, multiple frequency rheological technique to detect the gelation point at lower temperature was used and the data was subsequently extrapolated to higher temperatures based on the principles of cure kinetics to determine the gelation line as a function of temperature. Vitrification was determined based on the T_g–conversion relationship and isoconversional lines. Vitrification times were also directly measured by rheological experiments. Based on the gelation and vitrification times, a complete TTT cure diagram ranging from sol, gel, fully cured, glassy, and rubber states was constructed for the fast cure non conductive adhesive.

Keywords: Gelation; Vitrification; TTT cure diagram; Non-conductive adhesive; Flip chip

1. Introduction

As the electronic packaging requirements are driven towards smaller, higher density, and lower cost solutions, flip chip polymeric interconnects that provide an environmentally friendly solution for interconnections by replacing lead-based solder balls, are well positioned to meet these challenges. Being one of the solder-alternative polymeric interconnection technologies, non-conductive adhesives (NCAs) have many advantages such as easier processing, lower cost, and extendability to fine pitch applications. The conductivity of a NCA interconnect is completely dependent on the direct mechanical contact between the IC bump and the substrate pad. Cure stresses induced by cure shrinkage play an important role in the electrical connectivity and reliability of these interconnects [1]. Gelation and vitrification are two important events that occur during the crosslinking polymerization reaction characterized by the transformations of liquid-to-rubber and liquid or rubber-to-glass states, respectively [2,3]. At early stages of polymerization, shrinkage does not cause any stresses because of the flow nature and lack of any mechanical modulus of the liquid. After the critical gel point i.e. liquid-to-rubber-transition, the material begins to develop a significant modulus. If there is a constraint on the system boundary, constrain induced cure shrinkage stresses will develop. As the reaction proceeds, vitrification characterized by liquid or rubber-to-glass transition sets in and cure stresses develop monotonically with conversion after the vitrification point [4,5]. Therefore, the development of cure stress is highly related to the two events which also mark significant changes in mechanical stiffness. Therefore, a good understanding of curing process which involves time–temperature transformation (TTT) is of great importance for providing an optimal cure schedule.

Although there are many reports on the methodology of generating a TTT cure diagram of a variety of thermosetting polymers, the methodology of generating a fast cure material is still lacking, possibly due to equipment limitations. In the present work, the gelation and vitrfication transformations during cure of an epoxy based fast cure non-conductive adhesive are examined and a detailed TTT diagrams are presented.

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2. Experimental

The NCA used in this study was an epoxy based adhesive, XS8436 supplied by NAMICS Japan. To measure the gelation point of NCAs, ARES rheometer equipped with a dual range force rebalance transducer was utilized in the parallel plates geometry (disposable plates of diameter 20 mm, and 1 mm sample thickness), with air convection temperature control (accuracy ±0.1 °C). The temperature of the sample was measured by inserting a thermocouple probe inside the rheometer shaft. The plates were zeroed at the test temperature to ensure that the gap between the plates is consistent and the uncured adhesive was placed in between the plates with a gap of 1 mm. Multiple waveform dynamic tests for determining the gel point with a single measurement were performed from 80 to 100 °C. This consists of performing simultaneous time sweeps at different frequencies for a given temperature. The applied strain amplitude is 1% that is within the linear viscoelasticity (1% to 20% [6]) for each frequency.

Vitrification transitions were also studied by means of rheological measurements performed in the same rheometer with parallel plates of 20 mm diameter and samples of approximately 5 mm diameter and 1 mm thickness. A frequency of 1 Hz and a low strain (0.2%) were used due to the significant increase of stiffness during the vitrification process that could surpass the capacity of the transducer.

3. Results and discussion

3.1. Gelation

The gelation point is worthy to study because it is the onset of mechanical strength and cure stress. Moreover it is a termination point of voiding and resin bleed [7]. Gelation does not involve any chemical change in the curing process, and therefore cannot be detected by techniques sensitive to chemical reaction, such as DSC. However, the mechanical and rheological properties of the reaction medium do change during gelation, which can therefore be detected by methods based on changes in these properties. There are several methods available for determining the gelation point. Viscometry defines gelation time as the time at which the viscosity tends toward infinity [8,9], whereas torsional braid analysis (TBA) defines it as the time needed to reach the maximum $\tan\delta$. Thermal mechanical analysis (TMA) has been utilized to determine the gel time by applying a periodic force and the gel time was defined as the time required for the material to change from liquid to solid state [10]. By means of dynamic mechanical tests, gelation can be detected: (a) as the crossover of storage modulus and loss modulus where $\tan\delta = 1$ in ASTM standards (this is not necessarily true of all thermoset polymers) [11]; (b) as the point at which $\tan\delta$ becomes independent on the frequency by means of multi-frequency technique [6,12]. As can be seen from the above, there are many ways of defining gelation or gelation time. Curing times and gelation timesobtained through different techniques may not be directly compared [10]. Wherein, the gelation point is determined more precisely by the detection of $\tan\delta$ independent of measurement frequency.

Fig. 1 shows $\tan\delta$ measured by multiwave dynamic rheological method at 1, 5 and 10 Hz for isothermal cure temperature 100 °C. The point at which $\tan\delta$ is independent of frequency is clearly indicated as the gelation point and its corresponding time is regarded as gelation time. The gelation time at different cure temperatures is tabulated in Table 1. As can be seen from the table, gelation time will decrease with the increase of cure temperature. From the DSC measurement of the partially cured adhesives, it was found that the degree of cure at the gel point (α_{gel}) is 50 ± 5%.

3.2. Vitrification

Vitrification is a gradual, thermo-reversible process and its detection will vary with the technique employed. There are two main methodologies for the determination of vitrification, calorimetric and dynamic mechanical analysis. For calorimetric method, the material is cured at different times and temperatures. The T_g is determined by using DSC, TMA or DMA and the degree of conversion, by DSC, from residual heat. A single master curve T_g–degree of cure is then established. The time required to reach a given degree of conversion can be established through any of the classical kinetic procedures, since until vitrification the reaction is controlled chemically. Recently, the modulated density scanning calorimetry (MDSC) was used to directly determine the vitrification [13,14]. The second methodology consists of curing the sample by a technique which is sensitive to vitrification, such as TBA, DMTA, etc. Criteria of using rheological measurement include peak in $\tan\delta$ at 1 Hz peak in loss modulus at 1 Hz and [13].

To establish the relationship existing between the degree of cure and glass transition temperature, samples were partially cured at various times at cure temperature 90 °C, and the T_g of the partially cured material and degree of cure were then evaluated by means of a dynamic post curing. Fig. 2 shows the

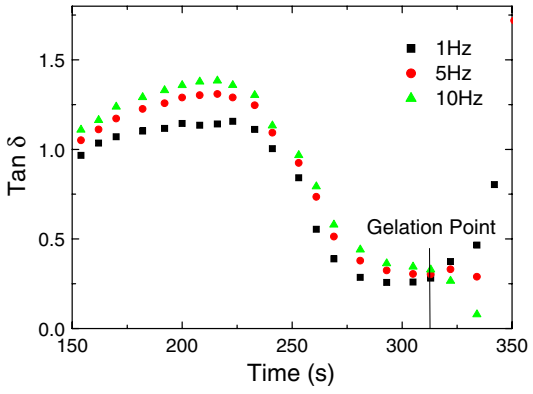

Fig. 1. Tan δ measured by multiwave dynamic rheological method at 1, 5 and 10 Hz during isothermal cure at 100 °C. The point at which $\tan\delta$ is independent of frequency is indicated as gelation point.