The effects of silica fillers on the gelation and vitrification of highly filled epoxy-amine thermosets

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SUMMARY: Highly filled thermosets are used in applications such as integrated circuit (IC) packaging. However, a detailed understanding of the effects of the fillers on the macroscopic cure properties is limited by the complex cure of such systems. This work systematically quantifies the effects of filler content on the kinetics, gelation and vitrification of a model silica-filled epoxy/amine system in order to begin to understand the role of the filler in IC packaging cure. At high cure temperatures (100°C and above) there appears to be no effect of fillers on cure kinetics and gelation and vitrification times. However, a decrease in the gelation and vitrification times and increase the reaction rate is seen with increasing filler content at low cure temperatures (60-90°C). An explanation for these results is given in terms of catalysation of the epoxy amine reaction by hydrogen donor species present on the silica surface and interfacial effects.

Introduction

Epoxy resins are used in many applications including encapsulation of microelectronic components. The encapsulation is responsible for providing protection for the microelectronic component from the surroundings, dissipating heat, and preserving the conductive connection between the device and the printed board. Important parameters in the encapsulation process are gelation and vitrification. At gelation the shear viscosity of the material is infinite, so all the wetting has to occur before gelation[1-3]. Vitrification is important because it provides the time for sufficient strength of the material so that it may be removed from the mould.

Fillers play an important role in encapsulation materials as they lower shrinkage on curing, decrease thermal expansion coefficients, improve thermal conductivity and lower the cost of the material[4]. However, due to the inherent reactivity of thermosets and the fact that fillers may modify the chemistry of the cure, filled epoxy resins are very complex materials and little is known about the effects of fillers on the cure and rheological characteristics of epoxy

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resins[5]. The aim of this paper is to describe the interactions between the filler and the reacting molecules and correlate these with the macroscopic cure properties of silica filled epoxy-amine systems.

Materials and Methods

The system studied was composed of diglycidyl ether of bisphenol-F (DGEBF) epoxy [PY306 Ciba-Geigy], cured with 4-4'-methylenedianiline (MDA) amine [Aldrich]. The silica filler is a high purity white crystalline silica flour [Commercial Minerals] with a mean diameter of 10 μm. Stoichiometric mixtures of epoxy-amine were prepared with 0, 10, 30 and 50wt% silica.

Gelation and vitrification times during isothermal cure were determined through rheological measurements on a Rheometrics RDSII rheometer. The geometry used was parallel plates (diamteters= 4 and 25mm and gaps=0.6 and 1.5mm). Multiwave Time Sweeps (frequencies=0.25, 0.5, 1.0, 2.0 and 4.0 Hz, strain=0.3% at each frequency) were used to determine the gelation and vitrification times. Dynamic strain sweep tests were performed to ensure the total strain chosen was within the linear viscoelastic region. Multiwave tests are advantageous for reactive systems as they allow the dynamic response to different frequencies to be analyzed instantaneously[6]. Gelation time is determined by the power law behaviour of dynamic moduli (G' and G") or, as a consequence, the point where the loss tangent (tan δ) is independent of frequency[7]. The peak in tan δ determines vitrification time[8]. Reaction rates and conversions along isothermal cure were determined through FTIR spectroscopy (Perkin Elmer FTIR System 2000) and DSC (TA DSC).

Results and Discussion

Table 1 summarises gelation and vitrification times obtained for 0, 10, 30 and 50% silica filled DGEBF/MDA at various isothermal cure temperatures (from 60 to 130°C). As can be seen for temperatures below 100°C there is a decrease in gelation and vitrification times with increase in filler level, but above 100°C there is no effect of filler level.

In order to determine if the difference in gelation and vitrification times observed is due to effects of filler on the cure kinetics, isothermal cure FTIR experiments were performed[9].

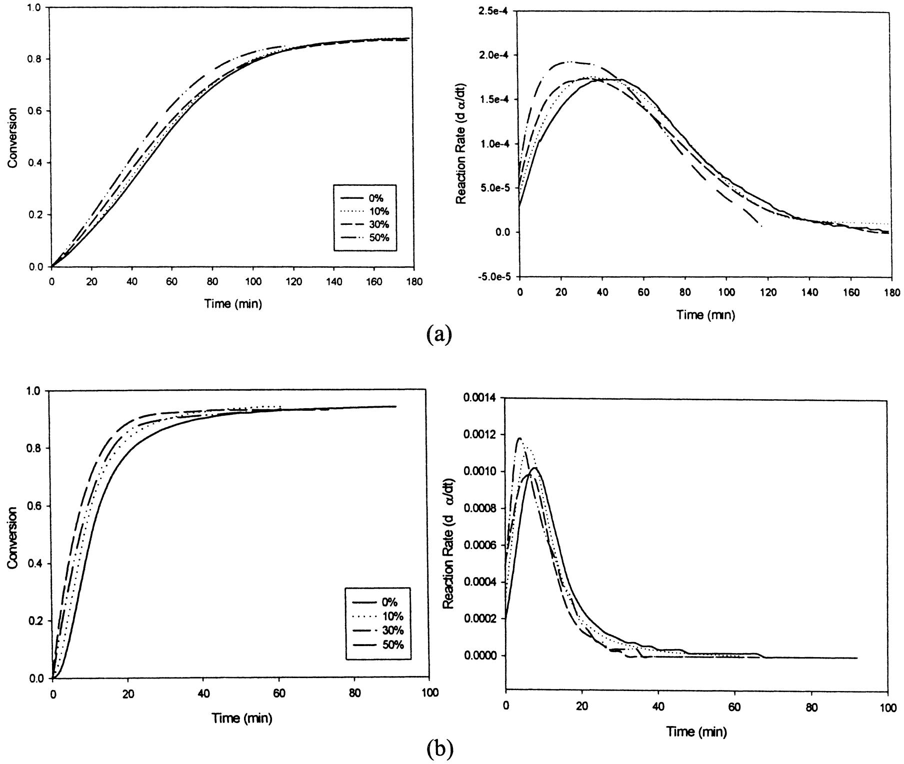
Figure 1 shows the effect of fillers on conversion and on reaction rate at (a) 80°C and (b) 120°C. These results suggest at 80°C that there is an increase in the rate of reaction for the highly filled systems especially at the initial stages of the cure. Results at 60, 70, and 90°C showed similar trends. However results at 120°C show minimal effects of fillers on the conversion or reaction rate (similar to results at 110 and 130°C).

Table 1: Gelation and vitrification times from rheological experiments.

	Gelation				Vitrification			
Temp. (°C)	0%	10%	30%	50%	0%	10%	30%	50%
60	222	222	190	163	240	240	220	187
70	150	142	115	102				
80	84	88	76	60	112	111	103	92
90	55	49	45	42				
100	38	38	32	29	57	55	54	48
110	22	24	23	21	45	46	39	41
120	16	16	16	15	40	39	38	36
130	12	12	12	13	36	37	37	35

A mechanistic kinetic model considering three possible reaction paths: (a) non-catalysed or impurity catalysed epoxy-amine reaction, (b) auto-catalysed reaction and (c) primary amine catalysed reaction accounting for different reactivity of primary and secondary amine was fitted to the isothermal experiments for the various filler levels. However, no good agreement with experimental data was obtained mainly due to two reasons: (a) loss of information when deriving functional group concentrations to calculate the reaction rates, and (b) the reaction mechanism is in fact more complex than the one suggested10).

Overall activation energies were then obtained from times to achieve rheological and theoretical gelation for the various temperatures. Theoretical gelation was considered to occur at 61.9% epoxide conversion which accounts for unequal reactivity of primary and secondary amine11) and which is suggested from the experimental data. Figure 2 shows the effect of filler on activation energy and pre-exponential factor (see Table 2 for values). From both rheological and kinetic data it is observed that filler decreases the activation energy and increases the pre-exponential factor. The activation energy for the unfilled system was 51 kJ/mol from FTIR data and 47 kJ/mol from rheological data and results from a combination of non-catalysed and auto-catalysed epoxy-amine reaction agreeing with previously reported results[10,12,13]. Current work is examining the relationship between activation energies and pre-exponential factors, in order to determine the true influence of fillers on reaction kinetics and energies and to elucidate the mechanism of filler interaction. Initial results showing a high correlation between the two parameters may be due to the oversimplification of one activation energy for the system and further modelling work is planned. Nevertheless, it is clear that both pre-exponential factors and activation energies are profoundly affected by filler content.



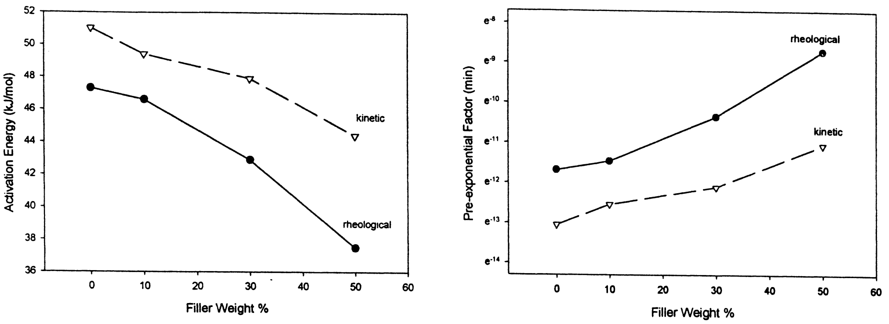
(a)

(b)

Fig. 1: Effect of filler content on conversion and reaction rate at (a) 80°C and (b) 120°C.

Table 2. Activation energies and pre-exponential factors.

	E_a (kJ/mol)		K_0 (min^{-1})	
Silica level	kinetic	Rheo.	kinetic	Rheo.
0%	51	47	$1.0e^{-13}$	$2.3e^{-12}$
10%	49	47	$3.2e^{-13}$	$4.0e^{-12}$
30%	48	43	$8.9e^{-13}$	$4.4e^{-11}$
50%	44	37	$8.8e^{-12}$	$1.7e^{-9}$



(a) (b)

Fig. 2: Effect of filler on (a) activation energies and (b) pre-exponential factor.

The decrease in the activation energy with increasing amount of silica could be through catalysis of the reaction by hydroxyl groups present on the silica surface. Figure 3 shows the FTIR spectra of the silica surface. The absorption peaks at 799 and 600 are due to in-plane bending vibrations of geminal hydroxyl groups on the silica surface[14)]. The absorption at 778 with a weaker absorption at 830 is probably due to isolated silanols[15)]. So there are indeed hydroxyl groups on the silica surface, which could be catalysing the reaction. However, the silica used is non-porous silica with a BET specific surface area of 1.6 m^2/g (small compared to 394 m^2/g for a mesoporous silica gel [Kieselgel 60][14)]). This small surface area would not be likely to explain the entire increase in reaction rate. Thus we believe that there is a complimentary effect of the filler on the reaction rate due to physical interactions between the filler and the monomers. Due to attractive forces between the silica and the monomers there is the formation of an interface region with a higher monomer concentration which results in a higher reaction rate. The effect is analogous to the work of Paz-Abuin et al.[12)], which explains the auto-acceleration of on epoxy-amine kinetics through a free-volume effect. In their work, they hypothesise that the volume occupied by the products of reaction (tertiary amines) diminishes the available volume for the reactants, increasing the "local" concentration of reagents and therefore the reaction rate. Here we hypothesise that the volume occupied by the filler particles, decreases the free volume in the system therefore increasing the local concentration of the activated complexes thus increasing the reaction rate. At higher temperatures, attractive forces are weaker, the size of the interface is smaller and there is less effect of filler on the reaction rate. In fact at infinite temperatures there are no attractive forces between the filler and the monomers, the molecules can move freely and the effect of the filler is actually to decrease the reaction rate due to dilution effect. This is confirmed by the pre-exponential factor, which increases with increasing amount of filler, that is, the system would gel at larger times for the higher filled systems at infinite temperature.

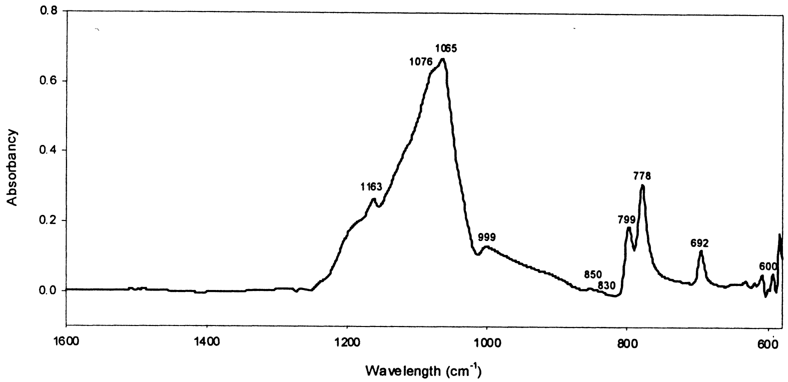


Fig. 3: FTIR spectrum of silica.

The same decrease in free volume due to the presence of filler that accelerates the reaction at its early stages is responsible for its deceleration at the later stages in the reaction as the reaction becomes diffusion control and the filler act as a barrier for diffusion.

The effect of filler on the activation energy as deduced from the rheological data is greater than that from FTIR conversions. That is, the filler is not only affecting the reaction kinetics but it is also favouring gelation at lower temperatures. This seems to add evidence to the existence of attractive forces between the filler and the matrix. If there were no attractive forces gelation would actually be delayed to higher conversion16).

Other investigations have reported a decrease in reaction rate due to addition of fillers17). The decrease is explained in terms of the higher thermal conductivity and heat capacity of the filler, which acts as a heat sink dissipating the heat of reaction and therefore reducing the reaction rate. This factor could be contributing to the reduced effect of fillers at high temperatures when the exotherm is higher and the temperature control is less efficient. The measured time for gelation is shorter than it would be if the temperature distribution were uniform, the effect being stronger for unfilled and lower filled samples. In this scenario, the resulting activation energy would be lower. As future work we hope to quantify this effect through a heat balance on both rheometer and FTIR device. Nevertheless, the fact remains that the filler accelerates the reaction and the effect can not be explained solely through catalytic effect of hydroxyl groups on the silica surface.

A time dependent Monte Carlo percolation algorithm is being developed in order to test the hypothesis described on this paper on the effects of filler on the network formation of epoxy-amine systems. The approach is to consider all possible reaction paths, including the filler catalysis, by assigning reaction probabilities for each event. The effect of the interface will be incorporated by positioning the molecules in the percolation grid according to their probabilities of encounter.

References

1. J. L. Stanford, M. J. A. Elwell, and A. J. Ryan, in *Processing of Polymers*, edited by H. E. H. Meijer, VHC Publishers, Weinheim 1997, p.465.
2. C. A. May, *Chemorheology of Thermosetting Polymers*, American Chemical Society, Washington DC 1983.
3. C. W. Macosko, *RIM: Fundamentals of Reaction Injection Moulding*, Hanser Publishers, Munich 1989.
4. K. W. Lem and C. D. Han, *J. Appl. Polym. Sci.* **28,** 3185 (1983).
5. P. J. Halley, *J. Appl. Polym. Sci.* **64,** 95 (1997).
6. E. E. Holley, S. K. Venkataraman, F. Chambon, and H. H. Winter, *J. Non-Newt.Fluid Mech.* **27,** 17 (1988).
7. H. H. Winter and F. Chambon, *J. Rheol.* **30,** 367 (1986).
8. D. Harran and A. Laudouard, J. *Appl. Polym. Sci.* **32,** 6043 (1986).
9. J. Mijovic and S. Andjelic, *Macromolecules* **28,** 2787 (1995).
10. S. W. Kim, M. G. Lu, and M. J. Shim, *Polymer Journal.* **30,** 90 (1998).
11. C. C. Riccardi and R. J. J. Williams, *Polymer* **27,** 913 (1986).
12. S. Paz-Abuin, A. Lopez-Quintela, M. P. Pellin, M. Varela, and P. Prendes, *J. Polym. Sci. Part A,* **36,** 1001 (1997).
13. J. Mijovic, A. Fishbain, and J. Wijaya, *Macromolecules* **25,** 979 (1992).
14. E. F. Vansant, P. Van Der Voort, and K. C. Vrancken, *Characterization and Chemical Modification of the Silica Surface*, Elsevier Publishers, Amsterdam 1995.
15. A. Burneau and J. P. Gallas, in *The Surface Properties of Silica*, edited by A. P. Legrand, Wiley & Sons Publishers, London 1998.
16. S. P. Yushanov, A. I. Isayev, and V. Y. Levin, *J. Polym. Sci. Part B* **34,** 2409 (1996).
17. S. H. McGee, *Polym. Eng. Sci.* **22,** 484 (1982).