Development of Reworkable Underfill From Hybrid Composite of Free Radical Polymerization System and Epoxy Resin

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Abstract—The application of the underfill encapsulant is to enhance the solder joint fatigue life in the flip chip assembly, typically up to an order of magnitude, as compared to the nonunderfilled devices. Most of the current underfills, however, are primarily thermosetting epoxy resin curing system based materials, which transform into an infusible three dimensional network structure, and exhibit appreciable adhesion and reliability, but lack of desirable reworkability after curing. From the standpoint of polymeric material chemistry, other thermoplastic or thermosetting polymer materials could be of great economic/cost interest as encapsulants for some microelectronic packaging applications. In this paper, the experimental focus was devoted to the study of adhesion, reliability and reworkability of the free radical polymerization (FRP) system, as well as its hybrid composites or blends with phenoxy resin or epoxy resin (EPR), which could be potential underfill materials. The study encompassed formulation screening based on adhesion measurement, and assessment on reliability and reworkability performance for selected compositions developed so far. Compared with common practice of synthesis of a new epoxy resin backbone or specialty polymer, these FRP/EPR hybrid composites from readily available raw materials would represent a cost effective approach toward reworkable underfill with good adhesion and reliability performance.

Index Terms—Adhesion, epoxy resin, free radical polymerization, hybrid composite/blend, interpenetrating polymer network, reliability, reworkable/reworkability, underfill.

I. INTRODUCTION

ORGANIC polymeric materials have found extensive applications in the microelectronics packaging industry [1], [2]. This has mainly been driven by their low cost compared to other packaging options and their capability to demonstrate the performance and reliability required for most applications. For example, amongst the different plastic packaging encapsulants, underfill is of significant interest for the flip chip assembly [3]–[6]. Due to the thermal expansion/contraction mismatch between the silicon die, solder bump and organic substrate, underfill reinforcement is essential in improving the integrity and reliability of the solder joints by an order of magnitude.

The most common chemistry for encapsulants in microelectronics packaging has been based on thermosetting epoxy curing systems. These materials provide excellent chemical resistance, electrical insulation, mechanical property, thermal stability and adhesion to various components. With different kinds of oligomeric resins and curing systems available, the epoxy chemistry has established itself with the unique customizing and processing possibility. However, the disadvantages could be rather poor shelf life in storage, long cure cycle under typical curing condition, as well as the issue of reworkability. Reworkable underfill has been one of the solutions to realize both cost consideration and reliability requirement for component, module and board level packaging [3]–[7].

The extensively practiced approach for a reworkable underfill is to synthesize a completely new epoxy backbone containing degradable linkage, either thermally or under effect of chemicals [8]–[19], or to employ specialty polymer [20]–[24] and additives [25], [26]. Another example would necessitate different processing from typical liquid dispensing [27]. In sharp contrast to those, we have been interested in developing low cost reworkable underfill from readily available raw materials. From the standpoint of polymeric materials, the category of thermoplastics and some of the thermosetting systems (other than common epoxy resin) could be of potential for use as microelectronic encapsulants. The thermoplastic materials could avoid the disadvantages of the thermosetting materials, e.g., the long curing process, lack of reworkability, etc. The free radical polymerization system, either thermoplastic or thermosetting, would be of interest to us due to its various monomer chemistry and initiating system from room temperature initiator to medium and high temperature initiator as well as irradiation (e.g., UV, etc.) sensitive initiator. The free radical polymerization is normally fast and the material properties are acceptable for most applications.

This paper describes the experimental studies on the adhesion performance of the thermoplastic and thermosetting free radical polymerization systems with different initiators, followed by the evaluation on reliability and reworkability for selected free radical polymerizable formulation and its combination with phenoxy resin or epoxy resin. Some of the hybrid composites containing 100% reactive liquids while prefilled with silica filler could exhibit fairly promising adhesion, reliability and reworkability.

II. EXPERIMENT

The free radical polymerization (FRP) systems investigated in this study included the mono-functional and di-functional double bond unsaturated monomers. The mono-functional monomer would give thermoplastic homopolymer upon curing, while the di-functional monomer would typically introduce crosslinkage into a thermosetting network. The monomers were designated sample names for the description hereafter: St, MMA, TPG, BMA and TPR for mono-functional ones, while DVB, EGDMA, TSG, BPADMA, and TSR for di-functional ones. The initiating systems used for these monomers were room temperature (RT, 25 °C), medium temperature (MT, typically 70 °C), high temperature (HT, typically 120 °C), and UV type initiators.

The other component in the hybrid composites was based on epoxy resin. A low molecular weight oligomer of poly(bisphenol A-co-epichlorohydrin) chemistry with two ends glycidyl capped was designated as EPR, which is a viscous liquid at room temperature. Another sample of EPRPH is a long chain poly(bisphenol A-co-epichlorohydrin), i.e., the so-called phenoxy resin, a thermoplastic polymer with nominal weight average molecular weight of about 40 000 determined by light scattering measurement, or number average molecular weight of about 8000 as estimated. For the polymerization of the epoxy resin, a liquid imidazole derivative 1-(CN-CH$_2$-CH$_2$-)-2-ethyl-4-methyl-imidazole, referred to as EMZ, was used at 4 parts by weight per 100 parts (phr) epoxy resin throughout the study. When the solid phenoxy resin was employed in formulation, a carrying solvent 2-butanone or methyl ethyl ketone (MEK) was used to dissolve the high molecular weight resin.

The glass transition temperature (T_g), storage modulus and coefficient of thermal expansion (CTE) for the cured formulation samples were measured with a TA Instrument DSC 2920 (modulation mode), DMA 2900 and TMA 2940, respectively. The heating rate was 5 °C/min for both DSC and TMA, and 3 °C/min for DMA.

The adhesion performance of the samples was characterized mainly with the die shear test: about 10 to 20 small pieces of SiN passivated die (2 × 2 mm) were assembled onto the same but larger wafer substrate (15 × 15 mm) with the samples applied between the interface as adhesives. To facilitate the test vehicle assembly procedure, no spacer was used at the die/substrate interface. Much attention was paid to the control of the material application and the uniformity of the sample preparation such as contact of die/substrate. The assembly of test vehicle was allowed to dry/cure at an appropriate temperature for the FRP initiator, followed by phenoxy/epoxy reaction (if EMZ was used) and post-curing following the prescribed curing schedule. The die shear tests were conducted on a Royce Instruments system 552 100 K module.

For reliability evaluation, the test vehicle first went through some accelerated aging process, 85 °C/85% RH conditioning or pressure cooking test (PCT) at 121 °C and 2 atmosphere, before the die shear testing was performed at room temperature. Liquid–liquid thermal shock (LLTS, −55 °C–125 °C with dwell time of 5 min. each) test was carried out with the formulation

TABLE I
DIE SHEAR STRENGTH FOR FREE RADICAL POLYMERIZED THERMOPLASTIC AND THERMOSETTING SYSTEMS

Thermoplastic	St	MMA	TPG	BMA	TPR
RT initiator	0 MPa	0 MPa	42.7 MPa	0 MPa	9.7 MPa
HT initiator	-	-	0 MPa	0 MPa	18.8 MPa
Thermosetting	St/DVB	MMA/EGDMA	TPG/TSG	BMA/BPADMA	TPR/TSR
RT initiator	0 MPa	0 MPa	7.9 MPa	-	-
HT initiator	-	-	20.1 MPa	8.3 Mpa	31.7 MPa

For thermosetting samples, monomers at 1/1 molar ratio.

under study as underfill applied to the assembly of 10 × 10 mm SiN passivated die on FR-4 substrate coated with solder mask, where glass beads of 75 microns size were loaded in the samples at 0.5 wt%. This was to simulate the actual standoff in typical flip-chip assembly. The appearance of underfill fillet crack or any other deterioration of the tested material was inspected with the naked eye as well as a microscopy.

The rework test was performed on a rework station or hot plate with a board working temperature from 210 °C to 180 °C. Once the die was pulled out of the underfilled site, underfill residue and solder mask delamination, if any, were observed and recorded. After cleaning and redressing the reworked site was ready for further process.

III. RESULTS AND DISCUSSION

A. Thermoplastic and Thermosetting FRP Systems

The monofunctional and difunctional unsaturated monomers discussed in the Section II are theoretically free radical polymerizable with either RT (room temperature) or HT (high temperature) initiator at the preselected loading concentration to give thermoplastic and thermosetting materials, respectively. However, this was not the case for the test vehicle assembly of die shear strength measurement, as summarized in Table I.

The systems of St and St/DVB, MMA and MMA/EGDMA revealed no measurable die shear strength with RT initiator. As a matter of fact, it was found that the materials applied between the die shear interfaces had already disappeared through evaporation within the initial curing at RT (before post-curing). Thus, for these systems, the HT initiator was not desired since it would require higher temperature to start the polymerization reaction. The evaporation of BMA monomer seemed to be limited at RT, but did occur upon the exposure to higher curing temperature, resulting in zero die shear strength. The monomer BPADMA appeared to have less evaporation tendency from the die shear interface (with HT initiator). All the above-mentioned systems were excluded for the following studies.

By contrast, the other monomers in Table I exhibited reasonable die shear strength with appropriate initiating systems. Monomers of TPG and TSG, TPR, and TSR are common in the fact that they all possess hydroxyl groups, which could act as anchoring sites toward the SiN substrate and thus hinder the evaporation of the monomers out of the die shear interface. From the above initial monomer screening test, we consider that TPG and TSG system is preferably applied with RT initiator for further tests in the paper, while HT initiator is normally employed for TPR and TSR system, unless otherwise indicated.
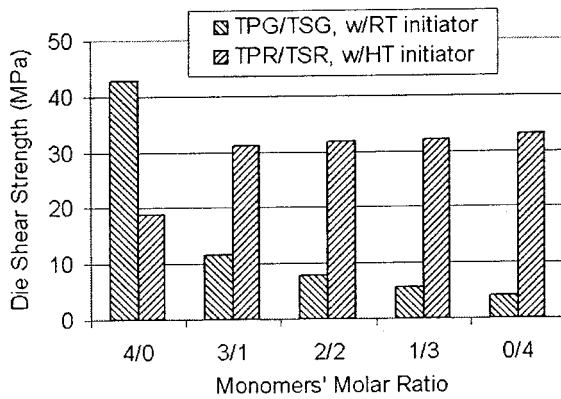
Fig. 1. Die shear strength as a function of crosslinking density for TPG/TSG and TPR/TSR system, initiated with RT and HT initiator, respectively.

TABLE II
GLASS TRANSITION TEMPERATURE AS A FUNCTION OF CROSSLINKING DENSITY

Initiator	Molar Ratio	4/0	3/1	2/2	1/3	0/4
RT initiator	TPG/TSG	80.4 °C	128.2 °C	Not detected with DSC up to 250 °C		
HT initiator	TPR/TSR	-7.6 °C	17.4 °C	86.3 °C	116.3 °C	131.6 °C

B. Effect of Crosslinking Density

Although either RT or HT initiator could be used to polymerize the free radical active monomers, we are interested in the effect of the nature of the cured materials upon the die shear strength performance, i.e., purely thermoplastic or thermosetting with different crosslinking density. This would be of help as to balance between material property and reworkability, as thermoplastic would be more favored for reworkability but may be deficient in adhesion or reliability performance. Thus, monofunctional TPG and di-functional TSG were combined at various molar ratios (4/0, 3/1, 2/2, 1/3, 0/4) with RT initiator, while TPR and TSR were mixed with HT initiator. However, these two systems displayed quite different behavior in die shear strength with varying crosslinking density, as shown in Fig. 1.

For the RT initiator polymerized TPG/TSG system, only the thermoplastic homopolymer of TPG could give reasonably high die shear strength. Any incorporation of the di-functional monomer TSG dramatically reduced the die shear strength, which decreased further with increasing crosslinking density. With the HT initiator for TPR/TSR system, the die shear strength exhibited some increase when moving from thermoplastic TPR homopolymer to crosslinked TPR/TSR copolymers.

Higher T_g values were always found for those two systems with higher crosslinking density, as listed in Table II. As observed for the current die shear test vehicle assembly with epoxy oligomers of various chain length, the flexibility and/or toughness of the cured materials played an important role in determining the die shear strength performance [28]. For TPG thermoplastic, being in the glassy state at RT with a T_g around 80 °C, the introduction of the di-functional TSG monomer would sure drive up the brittleness of the material. While the rubber-like TPR thermoplastic could only give limited die shear strength at RT, the crosslinking caused by the di-functional TSR monomer would reinforce the material matrix, yielding a higher die shear strength.
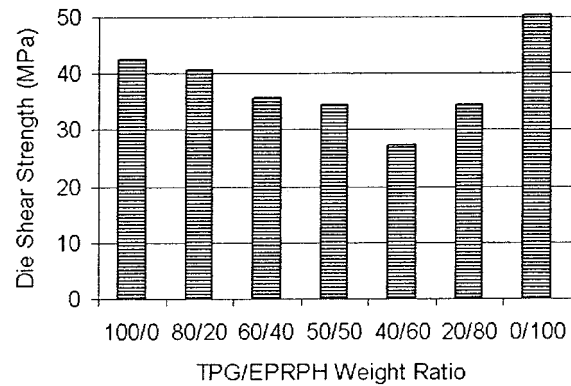

Fig. 2. Die shear strength for hybrid composites of TPG/phenoxy resin via solution assembly.

C. Hybrid Compositions of FRP With Phenoxy Resin

Since the die shear strength data obtained so far for free radical polymerization systems, as of either thermoplastic or thermosetting with either RT or HT initiator, were relatively lower compared with that from epoxy/phenoxy resin, we have decided to prepare hybrid composites of the free radical system with epoxy/phenoxy resin to take advantage of the epoxy/phenoxy resin. For this purpose, we first, for reworkability consideration, resorted to the preformed phenoxy resin (being thermoplastic without additional curing agent like EMZ) and RT initiated TPG thermoplastic system, which was applied to the die shear interface via the solution approach, i.e., the free radical polymerization system and the phenoxy resin was mixed with the solvent MEK at 30% solid content.

The die shear strength measured on these samples unexpectedly showed even lower values for the hybrid compositions than the pure parent materials, as displayed in Fig. 2. The reason for such observation could be, when the solvent gradually evaporated out of the die shear interface, the preformed phenoxy resin can restrict the free radical polymerization, rendering it into a diffusion controlled process from the very beginning of polymerization. This could limit the attainable conversion for the free radical polymerization component, and enhance the possibility for phase separation of the system. As a matter of fact, these hybrid materials (80/20 through 40/60 weight ratio) appeared turbid after curing except the sample of 20/80 weight ratio.

D. Effect of Chemical Compatibilizer and HT Initiator

For multiple phase systems [29], [30], interphase compatibilizer is believed to be effective in bringing the otherwise separated phases more miscible by acting as the bridging role across the phase interface. In order to favor the proceeding of the free radical polymerization, we may employ higher temperature for initiation and propagation by using HT initiator.

Fig. 3 shows the results with glycidyl methacrylate (GM) as the phase compatibilizer possessing both a double-bond unsaturation and an epoxide group; the former functionality could be activated for free radical co-polymerization, and the later could enhance the physical interaction and/or provide epoxide co-condensation with phenoxy resin (at the presence of a curing agent
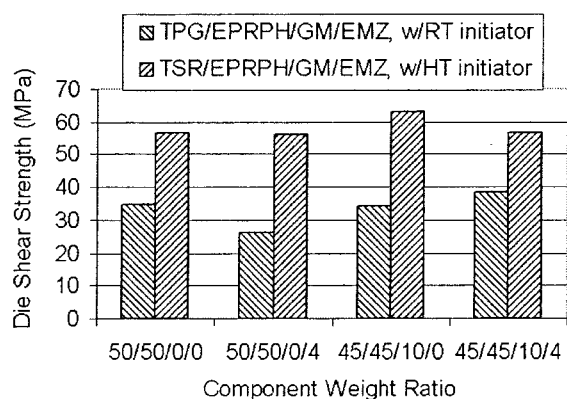
Fig. 3. Effect of interphase compatibilizer and system component composition on die shear strength.

Fig. 5. Die shear strength for TPG/EPR hybrid binder with various weight ratios: Effect of initiator and compatibilizer.
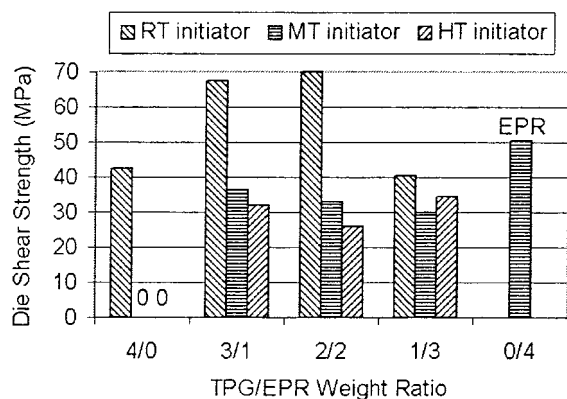

Fig. 4. Die shear strength for TPG/EPR hybrid binder with various weight ratios: Effect of RT, MT, and HT initiator (where EPR refers to pure EPR sample; "0" indicates zero die shear strength measured for pure TPG sample with MT and HT initiator).

Fig. 6. Die shear strength for TPR/EPR hybrid binder with various component weight ratios.

like EMZ), where again the solution approach was utilized with these systems for die shear test vehicle assembly.

It can be seen that, for the RT initiated system of thermoplastic TPG, starting with TPG/EPRPH at 50/50 weight ratio, the addition of the imidazole curing agent for the phenoxy resin worsened the die shear strength. This may be true if the already somewhat phase separated EPRPH phase continued to crosslink, which in-turn enhanced the phase separation condition. The introduction of GM into the systems without imidazole curing agent for the phenoxy resin had very little effect on the die shear strength, as the compatibilizer may have been incorporated into the TPG free radical polymerization phase, but not chemically bonded to the phenoxy resin phase. Further addition of the imidazole curing agents could actually establish the covalent links toward both TPG and phenoxy resin phase, thus giving rise to a somehow higher die shear strength. The addition of GM did not render these samples at such a specific weight ratio composition into fully transparency, possibly due to its amount as well as the curing schedule being not yet optimized.

Generally speaking, the hybrid composite from HT initiated thermosetting TSR with EPRPH exhibited higher die shear strength than that with RT initiated TPG thermoplastic system. For this free radical polymerization carried out at high temperature, the interphase compatibilizer seemed quite effective alone even without the imidazole curing agent for the phenoxy resin.
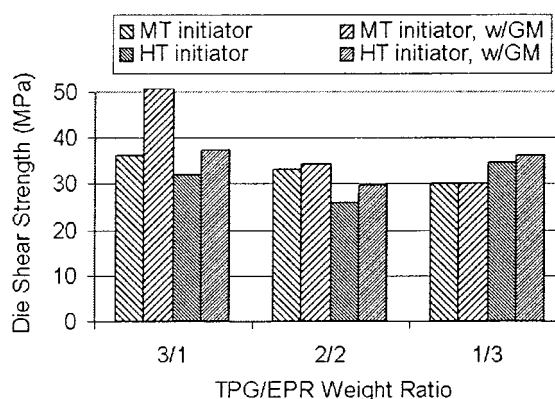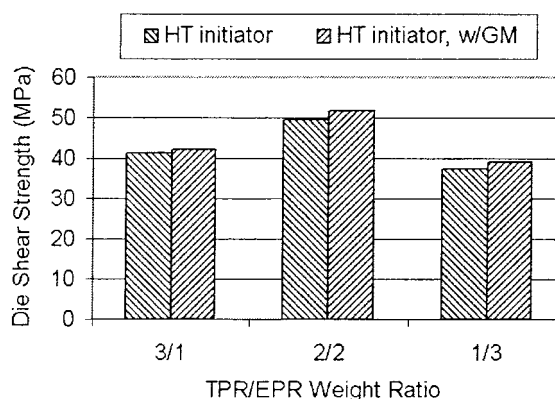
E. Development of Hybrid Composite Encapsulant Without Solvent

Starting from the thermoplastic and thermosetting free radical polymerization system, plus the in-situ polymerizable liquid epoxy resin (EPR) curing system to avoid the use of solvent as for the preformed phenoxy resin, we could develop hybrid composite encapsulants, taking the advantage from epoxy resin for higher adhesion performance, and potential reworkability capability from thermoplastic free radical polymerization system. These so-called interpenetrating polymer network [30] materials were 100% reactive liquids with rather low viscosity.

For this purpose, the TPG monomer was combined with EPR at various weight ratios (4/0, 3/1, 2/2, 1/3, 0/4); RT, MT, and HT initiators were employed for the free radical polymerization system, respectively, while EMZ was always used for liquid epoxy resin curing. The TPR monomer was also studied but only with HT initiator. For both monomers, the effect of the interphase compatibilizer of GM was investigated. The die shear strength results were depicted in Figs. 4–6.

When moving from RT to MT and then to HT initiator for the free radical polymerization component, the curing temperature for the TPG/EPR system went up accordingly, but the die shear strength decreased for most composition ratios studied (see Fig. 4). This could be explained by the fact that, because higher temperatures were needed to start the free radical polymerization from RT to MT and to HT initiator, the evapora-
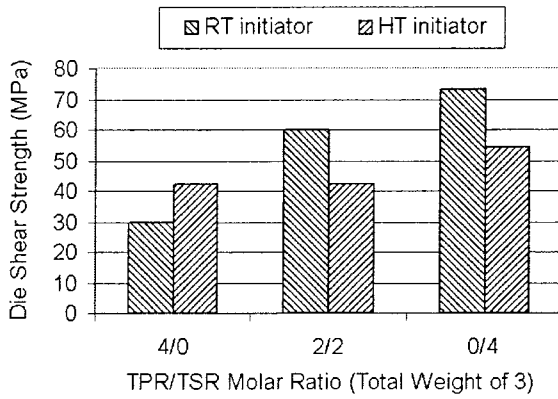
Fig. 7.   Die shear strength for TPR/TSR/EPR hybrids with weight ratio of 3 for TPR/TSR as total and 1 for EPR.

TABLE III
DIE SHEAR STRENGTH FROM HYBRID COMPOSITE WITH UV INITIATOR FOR FREE RADICAL POLYMERIZATION

TPG/EPR at 3/1 Weight Ratio		Die Shear Strength
w/o UV initiator	RT initiator	67.4 MPa
w/ UV initiator	No thermal initiator	68.4 MPa
w/ UV initiator	Plus HT initiator	58.0 MPa

TABLE IV
DESIGNATION FOR SELECTED HYBRID FORMULATIONS

FRP monomer component, wt	TPG			TPR		
	3	2	1	3	2	1
EPR component, wt	1	2	3	1	2	3
Un-filled version	UG3	UG2	UG1	UR3	UR2	UR1
Pre-filled version	PG3	PG2	PG1	PR3	PR2	PR1

tion of the free radical monomer became more severe. However, there was negligible evaporation of EPR oligomer and temperature effect on EPR curing. Fig. 5 clearly indicates that the addition of GM exhibited fairly large increase in die shear strength, and it appeared that such increase was more significant for systems containing more free radical polymerization component. The same held true if the polymerization of the free radical component proceeded that of EPR curing, i.e., with MT initiator, the free radical polymerization started well before the curing (about >115 °C) of EPR with EMZ curing agent.

When we used HT initiator for TPR/EPR hybrid composite, the free radical polymerization and the EPR condensation polymerization may take place at about the same time, and the introduction of GM gave rise to a rather limited effect on the die shear strength, as demonstrated in Fig. 6.

In an attempt to further learn the effect of crosslinking density of the free radical polymerization component for these hybrid composites, three parts of TPR/TSR mixture was combined with 1 part EPR (both by weight) while varying the monomer combination (TPR/TSR) molar ratio. It can be seen from Fig. 7 that, for those specific FRP monomers, the die shear strength from the hybrid composite increased with increasing crosslinking density brought by the di-functional TSR monomer, which was consistent with the results from pure free radical polymerization system (see Fig. 1).

F. Use of UV Initiator for FRP

As previously stated, some thermoplastic free radical polymerization and epoxy resin condensation hybrid composite of interest revealed rather high die shear strength with RT initiator. To limit the possible evaporation of monomers, we could take another approach of using a light sensitive initiator, e.g., a UV initiator. Table III lists some of the results obtained so far. The TPG/EPR hybrid composite at 3/1 weight ratio with UV initiator for FRP component could give rather high die shear strength, comparable to that from RT initiator.

It should be noted that the UV initiator might not be applicable for highly prefilled formulation, or for very large die size because of the restricted UV energy absorption within the flip chip standoff. Nevertheless, this may be overcome by employing thermal initiator for that part of the underfill underneath

the chip while using UV initiator for the rest dispensing material for fillet formation.

G. Reliability of Selected Hybrid Composite Formulations

Based on the adhesion results obtained so far, we have considered to transform the following into formulation manipulation, i.e., room temperature initiator for free radical polymerization, monomer TPG or TPR for thermoplastic FRP component, while EPR could be cured into thermosetting with EMZ. Interphase campatibilizer and silane coupling agent could also be included for improved performance. These formulations could be further prefilled with silica filler, typically at a loading level of 65 wt%, for enhanced material properties. Table IV summarizes the hybrid formulations intended for further study, i.e., FRP monomer TPG or TPR was combined with EPR at various weight ratios to give unfilled hybrid composite formulations as well as prefilled samples with silica filler. The silica filler would not increase the viscosity too much for the samples with those monomers, e.g., that of PG2 with 65 wt% silica filler was c.a. 3.6 PaS (3600 cps) at 25 °C measured on a TA Instrument rheometer with cone-plate configuration under a shear rate of 1 to 100 S^{-1}.

The material properties of these formulations could be found in Figs. 8–10. The TPG homopolymer would exhibit plastic characteristics at room temperature with a typical T_g of about 80 °C, while that of TPR homopolymer a bit below 0 °C. This could be clearly seen for the hybrid composites with different FRP/EPR weight ratios. With decreasing FRP component in the hybrid composition, the DSC T_g transition temperatures revealed increasing trend, which was quite consistent with results from other test methods like TMA and DMA (not shown). It can also be seen that the incorporation of silica filler greatly depressed the CTE below the transition temperature, and reinforced the hybrid composites by enhancement in the modulus of the materials.

Figs. 11 and 12 show the die shear strength of the prefilled FRP/EPR hybrid composites as well as the influence of pressure cooking test (PCT) and temperature/humidity aging. The as-assembled die shear strength of some formulations already surpassed that of the control sample, which was a typical commercially available epoxy based underfill. The PCT test at 121 °C and 2 atmosphere pressure exhibited more severe deterioration
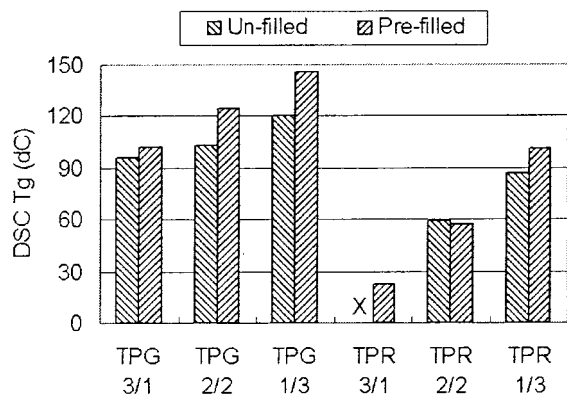
Fig. 8. DSC T_g for TPG/EPR and TPR/EPR hybrids (where "X" indicates no measurement was made for the unfilled TPR/EPR 3/1 sample).
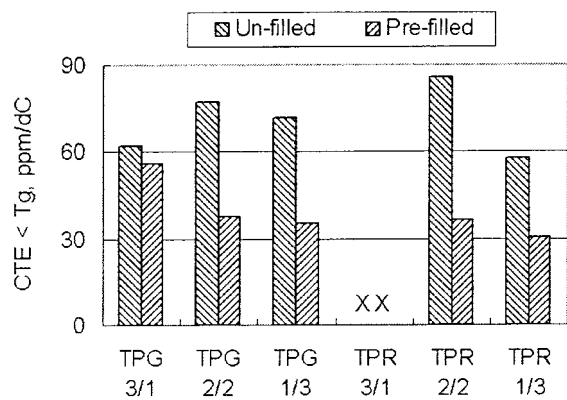

Fig. 9. CTE below T_g for TPG/EPR and TPR/EPR hybrids (where "X" indicates no measurement was made for the unfilled and prefilled TPR/EPR 3/1 sample).
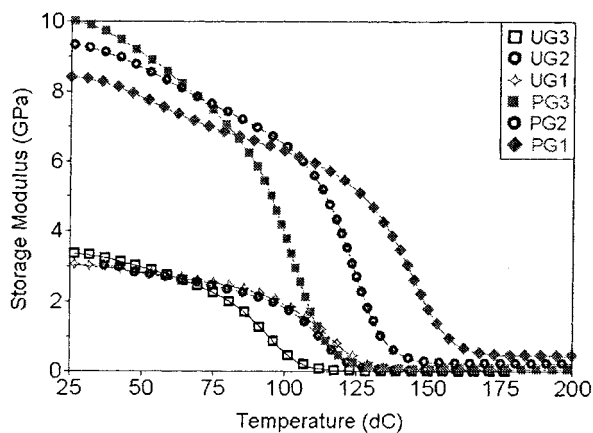

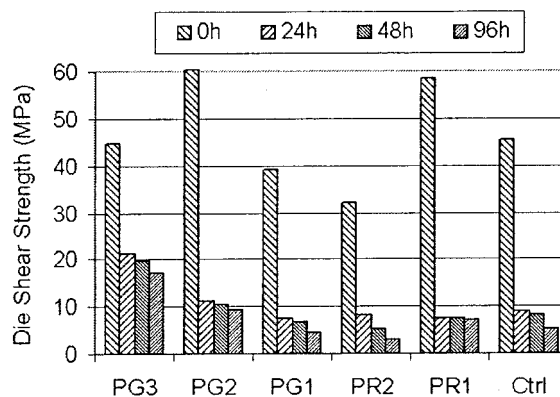Fig. 10. Reinforcement of TPG/EPR hybrids with silica filler.

Fig. 11. Effect of pressure cooking test aging on die shear strength of prefilled FRP/EPR hybrid formulations.

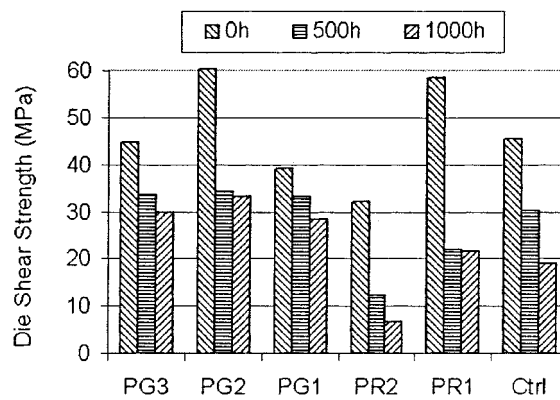Fig. 12. Effect of 85 °C/85% RH aging on die shear strength of prefilled FRP/EPR hybrid formulations.

TABLE V
LLTS RELIABILITY TEST RESULTS FOR HYBRID FORMULATIONS, CYCLES SURVIVED

Un-filled	UG3	UG2	UG1	UR3	UR2	UR1
LLTS	<800	<900	<800	·	<400	<800
Pre-filled	PG3	PG2	PG1	PR3	PR2	PR1
LLTS	>1000	>1000	>1000	<200	>1000	>1000

on the adhesion than the 85 °C/85% RH aging. Nevertheless, by the end of both tests, some of the formulations, especially those containing the plastic FRP component (TPG), retained much higher adhesion than the control sample.

These prefilled FRP/EPR hybrid composites were also applied as underfill and subjected to the LLTS test. The antifillet crack and antidelamination enhancement in reliability performance could be found in Table V. The unfilled materials all failed before the intended 1000 cycles in LLTS test with delamination and/or fillet crack observed, while the prefilled coun-

terparts could survive the 1000 thermal shock cycles without problem, except the sample of PR3, which might be attributed to its rather low mechanical property. This would fully support the approach of prefilling the organic hybrid binder with silica filler.

H. Reworkability of Selected Hybrid Composite Formulations

Bearing in mind that, the system of FRP/EPR mentioned above was actually thermoplastic TPG or TPR component plus thermosetting EPR. This could imply a good potential of reworkability for the materials. Only the prefilled samples that had passed 1000 cycles of LLTS test were taken for the rework test. One set of the test vehicle was the same as those for LLTS test; another set was PB8 peripheral daisy chain die from Flip Chip Technology assembled on corresponding substrate with eutectic Sn/Pb solder.

Although the formulations revealed thermal degradation in air at a temperature up to ~400 °C as in Fig. 13 from TGA test, they all demonstrated rework feasibility at a rework tem-
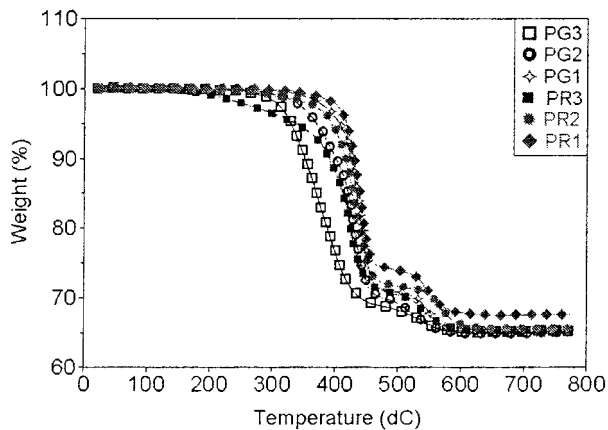
Fig. 13. Thermogravimetric graphs for prefilled FRP/EPR hybrid formulations.

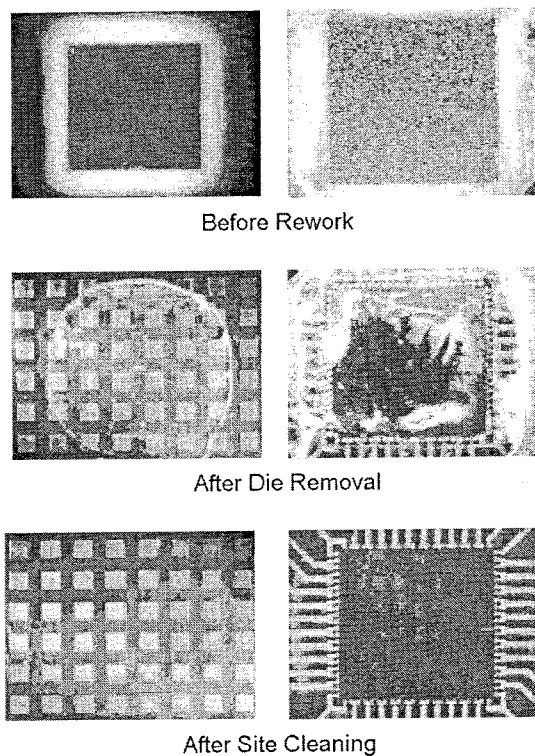Before Rework

After Die Removal

After Site Cleaning

Fig. 14. Rework process snapshots for simulated (left column) and solder jointed (right column) assembly.

perature of 210 °C for both types of test vehicle, and even as low as 180 °C for some formulations when there were no solder joints. As a matter of fact, this could be due to their rather limited mechanical property above the glass transition temperature (see Figs. 8 and 10). Fig. 14 shows the pictures of the rework process for the PG2 formulation sample. Thus, reworkability was considered successfully achieved for the prefilled hybrid composites developed so far.

IV. CONCLUSION

The thermoplastic and thermosetting free radical polymerization systems were investigated to apply as underfill encapsulants. The die shear strength of the formulation was measured with typical test vehicle assembly, followed by the study on the effect of crosslinking density on adhesion performance. The free radical polymerization system was then combined with advanced phenoxy resin as well as basic liquid epoxy resin to form hybrid composition materials. Different initiators, room temperature, medium temperature and high temperature as well as UV initiator, for free radical polymerization were employed. The influence from the chemical interphase compatibilizer was observed, which could be utilized to enhance the adhesion capability.

From the adhesion evaluation by the die shear strength testing, some experimental formulations of free radical polymerization and liquid epoxy resin hybrid composites were further elaborated for reliability and reworkability test. Liquid–liquid thermal shock, 85 °C/85% RH aging and pressure cooking test were carried out for them, bench-marked with typical commercial epoxy underfill sample. Thermal mechanical property was measured for both unfilled and prefilled versions. They could be correlated well with the results from reliability and rework tests.

Thus, it is expected to develop applicable hybrid composites consisting of free radical polymerization component, preferably thermoplastic in nature, and liquid epoxy resin, being thermosetting after curing. These hybrid materials as of 100% reactive liquid would exhibit good adhesion and reliability, mainly from the epoxy resin part, as well as practical reworkability, as pertaining to the free radical polymerization component. Because of the ready availability of the chemicals for the described hybrid composites, this approach represents a rather low cost material option toward reworkable underfill encapsulants with desired adhesion and reliability performance. With different choices of starting chemicals, especially the FRP component, these hybrid composites could be used for other encapsulation purpose in microelectronic packaging applications.

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