

Property and Reliability of Liquid Underfill Material for IC Packaging

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ABSTRACT: Thermoplastic nylon powder was added to naphthalene epoxy to serve as a stress release agent to reduce the stress resulting from the shrinkage during the cure of naphthalene epoxy. The purpose of this study was to explore the physical impact and effect on the forming object after adding nylon powder onto naphthalene epoxy. Mechanical properties were explored through the Izod impact test, the three-point bending test, tensile test, and lap shear adhesion test. Thermal mechanical analysis (TMA) and dynamic mechanical analysis (DMA) were conducted to identify the coefficient of thermal expansion (CTE) and the glass transition temperature (T_g). The rate of water absorption was measured via a test of pressure cook test (PCT), and insulation resist-

ance was assessed through the breakdown voltage experiment. The results indicate that the addition of nylon powder increases the fracture energy of the cured epoxy; however, mechanical properties (lap shear strength, flexural strength, tensile strength) decreased slightly. The TMA and DMA results showed that the CTE (α_l) decreased when nylon was added and the heat resistance decreased a little. The water absorption rate test and PCT showed that the rate of water absorption increased to a small extent, whereas the breakdown voltage decreased slightly. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3504–3509, 2006

Key words: blending; thermoplastics; thermosets; toughness

INTRODUCTION

Epoxy resin is characterized by the features of excellent adhesion, superb stability, small shrinkage, outstanding mechanical and insulation properties, and resistance against solvents, acid, alkaline, water, etc. Consequently, it is considered as a good material for IC packaging. Nevertheless, the defect of brittleness resulting from high crosslinking leads to the increased failure rate of IC elements. As IC devices are developing towards highly populated and small-scaled packages, requirements for low stress and brittleness-resistant material are becoming even stricter. As a result, elements like low moisture absorption, low coefficient of thermal expansion (CTE), and good heat resistance, etc. will be critical to evaluate materials.

Recently, silicone rubber has been applied to improve the toughness and lower the stress of packaging material^{1–3} because it can maintain the original properties of heat resistance and thermal stress; however, silicone rubber is incompatible with epoxy resins from the thermodynamic perspective. And, compatibility needs to be increased by other techniques like introducing a phenyl group to silicone rubber, combining silicone rubber with amino or epoxy functional

group to form block copolymer with epoxy resin, or adding polyether, etc.

As tenacious thermoplastic epoxy resins had already laid a good foundation,^{4,5} some studies were reported of using thermoplastic resins, like PES, PEI, PBT, and core-shell particles of PBA–PMMA to achieve the special modification performance. Most of the papers were concerning about the effect of different modifiers by physical or chemical modifications. To achieve the goal of low stress and low CTE, we used the difunctional naphthalene epoxy to react with acid anhydride in our research. It has features of a lower viscosity, a low CTE, and excellent heat and moisture resistance than other types of epoxy.

The approach of physically blending the solid nylon powder of a low melting point was adopted in this study to serve as the toughness and stress release modifier. For the process of manufacturing liquid underfill material for flip chip of IC package, this method is not only convenient and quick, but is also expected to increase the impact and fracture energy of the underfill material, which modifies epoxy resin, reduces the inner stress, and maintains heat resistance of the underfill material. As a result, the effect of adding nylon powder to naphthalene epoxy formed products is discussed in this research. For the experiment, Izod impact, the 3-point bending, and the adhesive strength tests were utilized to explore the mechanical properties. The impact of adding nylon to epoxy resin

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was probed. The effect of the glass transition temperature (T_g) was evaluated by conducting the dynamic mechanical analysis (DMA). The effects of the CTE as well as physical and chemical properties were explored through the thermal mechanical analysis (TMA), the pressure cook test (PCT), and the moisture absorption tests. The impact upon insulation resistance was assessed via the breakdown voltage (BDV) experiment.

EXPERIMENTAL

Materials

The materials used herein include naphthalene epoxy resins, product name EPICLON HP-4032D (epoxy equivalent weight = 140 g/eq), from DIC, and methyl tetrahydro phthalic anhydride as hardener, *N,N*-dimethylbenzylamine as accelerator, nylon powder from Toray Co., Japan, product name SP500, white powder with a particle size of 6.5 μm , m.p. 159°C, and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (particle size 2.6 μm) from Schill+Seilacher, Germany, as flame retardant. Fused silica (particle size 5.9 μm) was supplied from Fukusima Kiln Co., Japan. 3-Glycidylxypropyltrimethoxysilane, $\text{C}_9\text{H}_{20}\text{O}_5\text{Si}$, from Tokyo Kasei Industrial Co., was used as coupling agent.

Sample preparations

Based on Table I, each formula was mixed with a mixer for 10 min at 5000 rpm. After that, the mixture was injected into the mold and placed in the oven to cure at 150°C for 3 h. The samples were then cut into the test specimens as required.

Measurement

A Brookfield viscometer was used to measure viscosity changes of different combinations at different temperatures. For testing the flexural strength and flexural modulus, the test piece was trimmed to a size of $3 \times 12.7 \times 127 \text{ mm}^3$, according to ASTM D 790 and the span interval was set as 50 mm through the 3-point bending test. The test was conducted with a velocity of 1.2 mm/min at room temperature via a universal

strength testing machine. The acquired strength and the modulus can be calculated with the formula as follows:

$$\sigma = 3PL/2bd^2$$

$$EL^3/4bd^3 \times P/y$$

where σ is stress, E is the flexural modulus, L is the distance between test pieces, P is the maximum destructive power, b is the width of test piece, d is the thickness of test piece, and y is the deflection at load point.

For testing the Izod impact, the test was conducted with a V-shaped test piece of 1/8 in. (3/2 mm) thickness and of 2.54 mm in the gap depth of the notch at room temperature. The acquired destructive energy can be calculated via the following formula:

$$A = E/b(t - d) \times 1000$$

where A is the destructive power, E is the absorption power, b is the width of test piece, t is the thickness of test piece, and d is the depth of the V-shaped notch.

For testing the lap shear adhesive strength, the resin was applied between two aluminum pieces of $2.54 \times 10 \text{ cm}^2$, and the thickness of resin was controlled at 1 mm for each test specimen. The adhesion area was controlled within $2.54 \times 1 \text{ cm}^2$. The test specimen was preheated at 90°C for 3 min and then cured at 150°C for 2 h. After cooling down to room temperature, the test was conducted with a velocity of 1.3 mm/min via the universal strength testing machine according to ASTM D 1002. For the DMA, we apply DMA, TA-983 manufactured by Du Pont, to the resin of $50 \times 10 \times 2 \text{ mm}^3$ that is under a resonance frequency of 1 Hz, with temperature increasing at the rate of 5°C/min. The range is from room temperature to 250°C. For thermal mechanical analysis, the test was conducted with the test piece trimmed into a size of $6 \times 6 \times 2 \text{ mm}^3$ at a rising temperature of 10°C/min. The range is from room temperature to 250°C. For thermal gravity analysis, we use the model ULVAC TGD 700RH thermal gravity analyzer (TGA) to conduct the test under nitrogen at an increasing temperature of 20°C/min. The range is from 30 to 600°C. For testing the water absorption rate, the test piece was trimmed to a size of $3 \times 5 \times 5 \text{ mm}^3$, placed in a dryer for 2 h, and removed to weigh. It was put in a humidity chamber at 85°C and 85% relative humidity. The weight was measured after 100 h. Water absorption rate = [(weight after 100 h – weight removed from the dryer)/weight removed from the dryer] \times 100. For the PCT, the test piece was trimmed to a size of $3 \times 5 \times 5 \text{ mm}^3$, placed in a dryer for 2 h, and removed to weigh. The temperature was set at 121°C and the pressure at 2 atm. The weight was measured after 24 h. Water absorption rate = [(weight after 24 h – weight removed from the dryer)/weight removed from the

TABLE I
Component Formula

Component	Component formula ^a				
	1	2	3	4	5
Epoxy	100	100	100	100	100
Hardener	115	115	115	115	115
Accelerator	1	1	1	1	1
Fused silica	300	300	300	300	300
Flame retardant	6	6	6	6	6
Nylon powder	0	5	10	15	20
Coupling agent	6	6	6	6	6

^a All compositions are in grams.

dryer] $\times 100$. For BDV testing, the test piece was trimmed to a size of $75 \times 75 \times 5 \text{ mm}^3$ and the test conducted with an increasing voltage rate of 500 V/s until current penetrates. The oxygen index (OI) was measured by a Limit Oxygen Index Tester, Polymer Laboratories, HFTA II, 20 s after the ignition. According to the ASTM D 2863 standard, the specimens were cut into sizes of $125 \text{ mm} \times 6.5 \text{ mm}$, 3.5 mm thickness. The definition of OI is "the minimum concentration of oxygen to maintain a candle-like burning for a testing material under an environment with slowly rising gas of nitrogen/oxygen mixture." The thermal equilibrium is established between the heat released when the specimen burns and the heat loss from the testing environment. The OI of a testing material therefore can be identified either by a specific burning time period (3 min) or by a specific burned length of the specimen (50 mm, 75 mm). The OI then is defined as:

$$[\text{OI}] \% = \frac{[\text{O}_2]}{[\text{O}_2] + [\text{N}_2]} \times 100\%$$

where $[\text{O}_2]$ is the volumetric flow rate of O_2 (cm^3/s) and $[\text{N}_2]$ is the volumetric flow rate of N_2 (cm^3/s).

RESULTS AND DISCUSSION

The underfill material used for flip chip IC packaging has to be characterized with lower viscosity, lower stress, excellent mechanical strength, heat resistance, low water absorption rate, and good adhesive strength. The impact on physical property, thermal resistance, and insulation by adding nylon powder is discussed below:

Working viscosity of liquid underfill material

The naphthalene epoxy used in the experiment is a semisolid resin at room temperature. When the temperature rises, the viscosity decreases sharply, as shown in Figure 1. The viscosity was 276,200 cP at 25°C

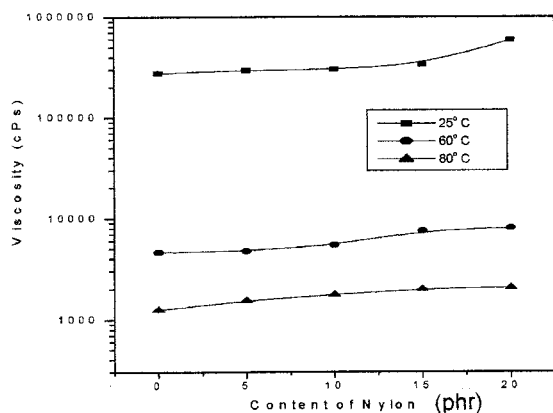


Figure 1 Relationship between viscosity and different contents of nylon at 25, 60, and 80°C.

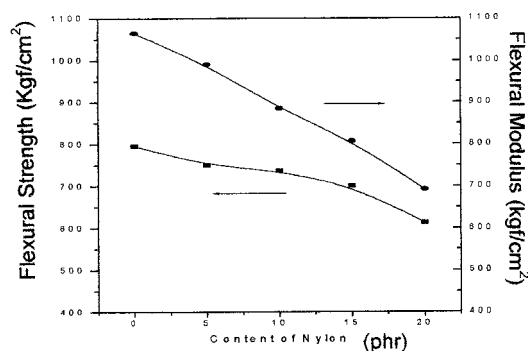


Figure 2 Relationship between flexural strength and flexural modulus with different contents of nylon.

and reduced to 4,600 cP at 60°C and 1250 cP at 80°C before adding nylon powder.

Addition of nylon powder increases the viscosity of resins and a proper working temperature (like 80°C) may be located from the aforesaid experimental data.

Dynamic impact imposed by nylon

The relationship between the flexural strength and the amount of nylon powder is shown in Figure 2. After adding nylon, the flexural strength decreases slightly to between 0 and 15 phr of nylon, which might be resulted from a lower density of crosslinking network compared to that of pure epoxy.⁶ The strength reduces to a maximum extent between 15 and 20 phr. The relationship between the flexural modulus and the amount of nylon powder is also shown in Figure 2. The modulus decreases as more nylon is added, which indicates that it is tougher than pure epoxy. Nylon has a linear structure and disperses in the epoxy matrix. It shows local shear deformation when it is under external force. This will increase the toughness of the material.

The relationship between the fracture energy in Izod impact test and the amount of nylon powder is shown in Figure 3. The crosslinking density of epoxy reduces

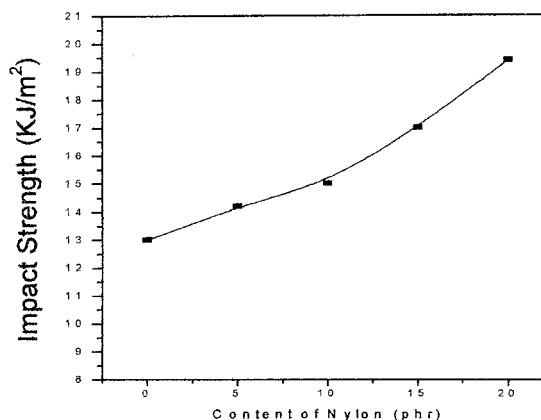


Figure 3 Relationship between Izod impact test and different contents of nylon.

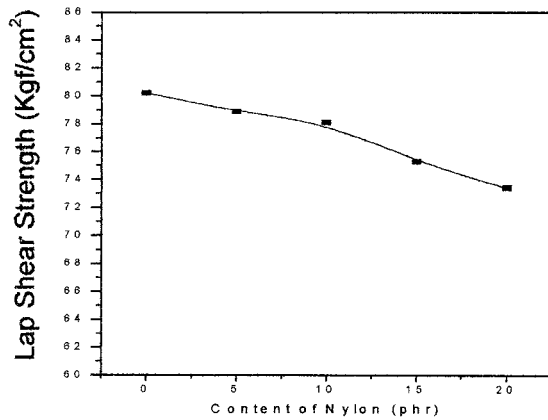


Figure 4 Relationship between adhesion strength and different contents of nylon.

as more nylon is added, which makes the material tougher and increases its fracture energy.

As nylon is added, the lap shear adhesive strength reduces, as shown in Figure 4. Since the molecular weight of nylon is greater, viscosity becomes greater after melting; therefore, when nylon is added, the wetting ability of material becomes worse and adhesion is reduced as well. In addition, as nylon has worse adhesive strength than that of epoxy, nylon-dominant effect is revealed with more nylon in the system.

Glass transition temperature (T_g) effect imposed by nylon

The relationship between $\tan \delta$ of DMA and the temperature is shown in Figure 5. The α , the transition peak, in the figure refers to the glass transition point of integral epoxy (T_g). T_g of nylon is 55.6°C and naphthalene epoxy is 136°C. After adding nylon powder, T_g reduces a little bit. As it reaches to 20 phr, T_g decreases to 123.6°C. T_g of epoxy is affected by crosslink density

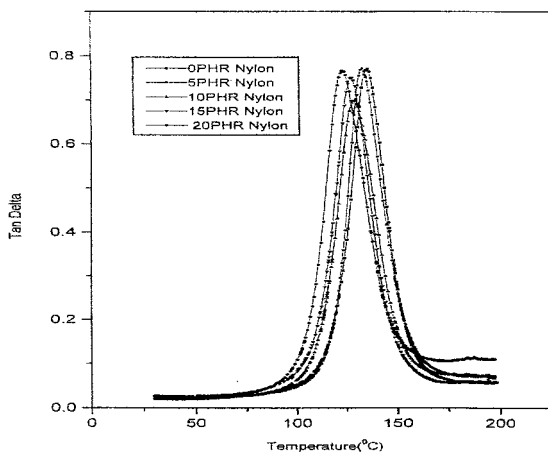


Figure 5 Analysis chart of dynamic viscoelasticity on adding different contents of nylon.

TABLE II
 T_g Data Acquired from DMA Testing

Component	T_g (°C)
Nylon	55.6
Epoxy	136.0
5 phr nylon	133.8
10 phr nylon	129.5
15 phr nylon	127.6
20 phr nylon	123.6

after curing because it limits segmental mobility of polymer chains. As more nylon powder is added, the crosslink density is lowered, which leads to reduction of T_g . In Table II is shown T_g of epoxy with different contents of nylon powder.

Furthermore, polymer molecules begin to move as temperature is increased, which causes linear volume expansion. The CTE is called α_1 . When the temperature reaches the glass transition temperature, the material changes from the glassy state to the rubber state, which makes the volume expand freely and rapidly. A turning point appears at this moment. As the temperature keeps increasing, the material keeps on expanding and the CTE is called α_2 , which is greater than α_1 . Results of the acquired T_g and CTEs are shown in Table III.

According to the TMA results, it is known that the T_g of formed material reduces as nylon is added, which coincides with that of the DMA testing.

Impact upon physical property imposed by nylon

Based on the results shown in Table III, the CTE decreases as nylon powder is added. However, when nylon powder with a greater CTE is used as the stress release agent, α_1 becomes smaller and smaller. As epoxy resin added with nylon powder varies in contracting level at processing temperature and room temperature after cooling, a radial tensile stress⁷ is produced on the interface between these two materials, which not only destroys the interface and forms cavitations, but also increases the local free volume between nylon and epoxy and makes CTE become greater as more nylon powder is added. If filler with a

TABLE III
 T_g and Coefficient of Thermal Expansion Acquired from TMA Testing

Component	T_g (°C)	α_1 (1/°C) $\times 10^{-6}$	α_2 (1/°C) $\times 10^{-6}$
0 phr nylon	118	48.5	115
5 phr nylon	117	43.5	92
10 phr nylon	114	35	87
15 phr nylon	110	33.5	84
20 phr nylon	106	33	69

low CTE is applied, the direction of the produced stress becomes opposite. The stress will decrease the local free volume between resin matrix and silica filler. As more nylon powder is added, such phenomenon becomes even more significant, which leads to reduction of the CTE.

In addition, as nylon changes from solid state to liquid state during the crosslinking reaction process, the volume will expand; however, epoxy resin produces contraction due to crosslinking reaction, whose stress offsets the expansion force produced by nylon exactly. Consequently, it is inferred that the contracting stress would be reduced after hardening nylon.

The relationship between the water absorption rate and nylon content is shown in Figure 6. As there is more nylon content, the water absorption rate increases because NHCO, a functional group of nylon, can be integrated with water easily, resulting from the hydrogen bonding. The water absorption rate plays a critical part in creating "popcorn effect" for IC elements. Nevertheless, as a limited quantity is added, the revealed effect is not great.

The relationship between the water absorption rate after PCT and nylon addition is also shown in Figure 6. The water absorption rate is affected by addition of nylon powder and becomes even higher than that in the previous test, which is because water molecules can enter the empty spaces inside the material more easily under high pressure.

Impact upon insulation destruction imposed by nylon

Results of BDV tests are listed in Table IV.

Insulation of the material decreases along with the addition of nylon because nylon can absorb water easily and has a lower insulation property than epoxy resin. As a result, BDV reduces as nylon increases.

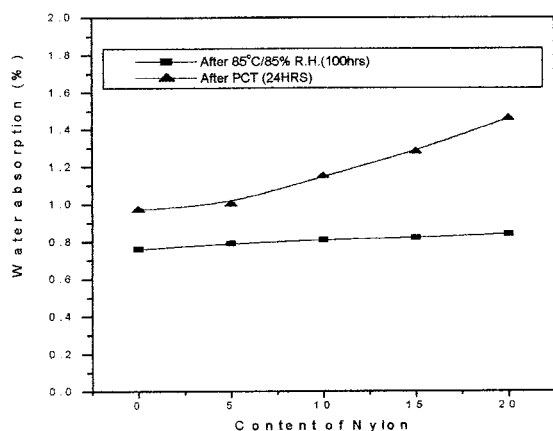


Figure 6 Water absorption rates at different contents of nylon.

TABLE IV
Breakdown Voltage at the Voltage Increasing Rate of 500 V/s

Component	Breakdown voltage (kV/mm)
0 phr nylon	19.7
5 phr nylon	15.8
10 phr nylon	13.4
15 phr nylon	11.3
20 phr nylon	10.3

The thermal pyrolysis and combustion behavior of naphthalene epoxy

The temperature changes in naphthalene epoxy thermal pyrolysis reaction after adding different concentrations of nylon powder were observed. From the thermal pyrolysis curve in Figure 7, we saw that the temperature for thermal pyrolysis was about 390–420°C, and the range was much higher than the epoxy curing temperature of 150°C. The thermal pyrolysis temperature was similar with different amounts of nylon powder. There were two benzene rings in the structure of naphthalene epoxy and its heat resistance was much better than that of nylon.

To evaluate flame retardation of epoxy in this study, OI is used. The larger value of OI, the harder it is for material to catch fire and to burn. Generally speaking, for the case of OI below 21, the material is considered as "flammable"; for OI = 22–25, the material is "self extinguishable"; and in the case that OI is above 26, the material is almost "hard to burn." The relationship between OI and different contents of nylon is shown in Figure 8. OI decreased when nylon powder was added because of the poor flame retardancy of nylon.

The OI of naphthalene epoxy, without flame retardant, silica and nylon, was 19.2. The OI reached 23.5 after adding 300 phr of silica filler. It reached 25.8 after adding 6 phr of flame retardant. The flame retardant

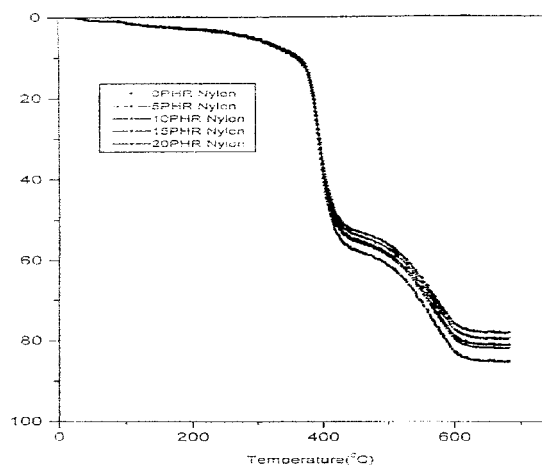


Figure 7 Analysis chart of thermogravimetry loss for materials with different contents of nylon.

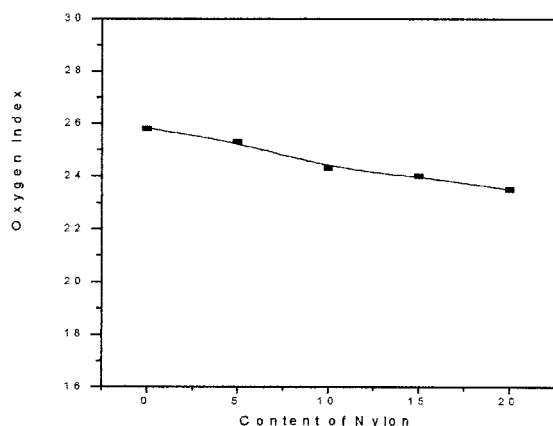


Figure 8 Relationship between OI and different contents of nylon.

has phosphorus and melamine structure. Its melamine group can form melam and melam-based chars with high thermal stability. We also discovered that as the flame retardant increased, the thermal pyrolysis temperature decreased. The flame retardant ability resulted from the layer of charcoal generated from reactions between epoxy and flame retardant during thermal pyrolysis.

On the other hand, 300 phr of silica filler was added into the epoxy because the addition of large amount of silica filler can improve its flame retardancy. In other words, both flame retardant and silica filler provided the improvements to the value of OI. In the research, the OI value could reach 25.8 when silica filler and flame retardant equaled to 300 and 6 phr respectively.

CONCLUSIONS

The advantages of using naphthalene epoxy resin as underfill material for IC packaging are low viscosity, high wetting ability, and excellent lap shear adhesive strength. In addition, a large amount of filler can be added to increase the strength, to decrease the CTE, flame retardancy, and to reduce the water absorption rate. Based on the results of 300 phr of filler in this study, material fracture energy was increased by adding nylon powder; however, mechanical property decreased slightly. According to the TMA results, it showed that the CTE (α_1) became lower as more nylon was added. The DMA experiment also revealed that heat resistance of the material was reduced to a small extent. The water absorption rate increased slightly in the water absorption test and PCT experiment. The insulation resistance test also indicated that the BDV decreased slightly.

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