Study on Preparation and Properties of Polyurethane-Based AlN Potting Compounds

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Abstract. Polyurethane (PU) is a widely used polymer material. Adhesives prepared with polyurethane as the base material can bond a variety of materials and have excellent performance. In the electronic packaging industry, the potting compounds prepared by using polyurethane as the base material and aluminum nitride powder as the thermally conductive filler has excellent thermal conductivity, which adapt to the increasingly miniaturization and high integration requirements of integrated circuits, and can dissipate the heat generated by components in time, which can keep the device in the best state during using and keep its efficiency and stability. With the continuous development of the microelectronics industry, the advantages of potting compounds with excellent thermal conductivity in the market will become more and more obvious.

1. Introduction
Polyurethane adhesive has excellent bonding performance and has advantages that cannot be matched by other materials, such as excellent chemical resistance, low temperature resistance and friction resistance. It is widely used in various fields such as aerospace, wood decoration, automotive sealants, etc [1]. However, polyurethane is a poor conductor of heat and can't meet the thermal conductivity requirements of the electronic packaging industry. If a filler with high thermal conductivity is added to the polyurethane matrix, such as aluminum nitride, a thermally conductive potting compound that meets the requirements of electronic packaging can be produced, and it can also meet the requirements of insulation. The thermal conductivity of normal size aluminum nitride is about 36 W/(m·K). While the thermal conductivity of nano-AlN can be as high as 320 W/(m·K), and with high dielectric strength and low dielectric loss. These excellent characteristics are important for improving the comprehensive properties of polyurethane-based encapsulants has great potential and value [2-5]. However, the nano-aluminum nitride powder not only has a large surface area, but also has a high surface activity. So it is very easy to agglomerate and easy to interact with moisture in the air. Therefore, the nano-aluminum nitride powder is used as the filler of the polyurethane-based potting compound, which needs to be modified.

Polyurethane as the raw materials for the preparation of potting compounds are generally selected from oligomeric polyols and diisocyanates and are prepared by stepwise addition polymerization by selecting appropriate chain extenders [6-7]. In general, it can also be prepared by a multi-step process by using a prepolymer as a springboard or a one-step process where two components are mixed together. In addition, polyurethane has a special chemical structure and excellent comprehensive performance. Polyurethane-based potting compounds can protect electronic components from gas and
liquid erosion, vibration damage, and dust and keep their efficiency and service life for these excellent properties [8-11].

In this paper, the preparation and performance of polyurethane-based AlN encapsulants are studied by using thermoplastic polyurethane (TPU) as the base material and 100 nm aluminum nitride (AlN) powder as the thermally conductive filler. And it will provide the experimental foundation and data support for the encapsulants in microelectronics industry in the future.

2. Experiment
The experimental procedures included modification of nano-aluminum nitride powder and preparation of thermally conductive potting compound.

2.1. Experimental Procedures of Modified Aluminum Nitride (AlN)
The titanate coupling agent was mixed with isopropanol in a certain proportion to prepare a titanate coupling agent solution. Then added AlN powder to the titanate coupling agent solution, and then leached after mechanically stir for a definite duration. Got the aluminum nitride powder rinsed with absolute ethanol several times while suction-filtering to ensure that there is no coupling agent remaining. Then it should be placed in a vacuum dryer at a certain temperature for a certain period of drying. After drying, got it out for using in the next steps.

2.2. Experimental Procedures of Preparing A Thermally Conductive Potting Compound
(1) The experimental device was set up with an iron support and fixed the three-necked flask above the oil bath pot and then put the stirring paddle in the middlemost port. Then got the condensing tube inserted at one of the bottle sides of the three-necked flask and used the other port as the feeding inlet. And fixed the digital display stirrer for mechanical stirring on the iron support.

(2) A certain amount of thermoplastic polyurethane (TPU) particles were weighed and got them into a three-necked flask with a certain volume of DMF (N,N-dimethylformamide) solution. Then got the feeding port sealed with a glass stopper and set a certain temperature of the oil bath and then got the digital display mixer turned on with a certain stirring speed until the TPU was completely dissolved.

(3) A certain amount of modified aluminum nitride (AlN) powder were weighed and got them into the three-necked flask and kept stirring for a certain period of time to ensure uniform mixing. Then got the three-necked flask removed and put it into an ultrasonic cleaner for ultrasonic dispersion for a certain period of time, and mechanical stirring was maintained during the period.

(4) Got the three-necked flask removed and sealed, and got a vacuum pumping operation performed on the mixed solution for a certain period of time. Then got the mixed solution poured into the corresponding mold, and placed it in a vacuum oven with a certain temperature for a certain period of time. Then took it out and saved it for testing.

(5) Got the mass of the added modified aluminum nitride (AlN) powder changed and repeated the above experiment, and got the prepared sample saved for testing.

The amount of experimental reagents and raw materials is shown in table 1.

**Table 1.** The amount of experimental reagents and raw materials.

| Modified AlN (g) | The mass fraction of AlN (%) | The mass of TPU (g) | The volume of DMF (ml) | Way of stirring                     |
|-----------------|------------------------------|--------------------|----------------------|-------------------------------------|
| 5.0             | 25.00                        | 15.0               | 60                   | Ultrasonic dispersion, mechanical stirring |
| 10.0            | 40.00                        | 15.0               | 60                   | Ultrasonic dispersion, mechanical stirring |
| 15.0            | 50.00                        | 15.0               | 60                   | Ultrasonic dispersion, mechanical stirring |
| 20.0            | 57.14                        | 15.0               | 60                   | Ultrasonic dispersion, mechanical stirring |
3. Experimental Results and Discussion

3.1. Conductivity Analysis
A semiconductor integrated tester was used to conduct conductivity test on the potting compound added with modified aluminum nitride (AlN) powder. The results are shown in figure 1.

![U-I curve of potting compound with different contents of modified AlN](image)

Figure 1. U-I curve of potting compound with different contents of modified AlN.

According to the U-I curve of potting compound with different contents of modified AlN in figure 1, we can get the volume resistivity of the potting compound under different mass of modified AlN as shown in table 2.

| Modified AlN (g) | 5.0  | 10.0 | 15.0 | 20.0 |
|-----------------|------|------|------|------|
| Volume resistivity (Ω·m) | 1.02×10⁹ | 9.16×10⁸ | 3.44×10⁸ | 1.27×10⁸ |

Table 2. Volume resistivity of the potting compound with different contents of modified AlN.

It can be seen from figure 1 and table 2 that the potting compound added with modified AlN powder was almost insulating. However, according to the curve in figure 1, it is not difficult to find that the conductivity of the potting compound tends to improve as the value of the mass fraction of modified AlN powder increasing. However, TPU and AlN powder are insulated and this phenomenon may be caused by the electron migration which caused by the small size effect of the nano aluminum nitride (AlN) powder. This characteristic provides a feasible way for improving the conductivity of materials.

3.2. Thermal Analysis
(1) TG test analysis
It can be found from figure 2 that the thermal stability of the potting compound was getting better and better with the increasing mass of AlN. At about 300 °C, the mass of the potting compound began to decrease sharply. With the increase of temperature, the mass dropped sharply again around 370-400 °C, and the performance was relatively gentle after 450 °C. The changes of the mass of the potting compound can be divided into four stages comparing with the pure TPU samples with no aluminum nitride powder added. They were the early stable stage, the early dramatic change stage, the middle dramatic change stage and the last stable change stage. Pure TPU can only be divided into three stages. They were the early stable stage, the middle dramatic change stage and the last stable stage. So it was not difficult to find that the addition of AlN has a great effect on improving the thermal stability of the potting compound. And the more the amount of AlN was added, the more obvious this effect was.
Figure 2. TG diagram of potting compound with different contents of modified AlN.

(2) Thermal conductivity test analysis
It can be obtained that the thermal conductivity of the potting compounds at 50 ℃ according to the results of the thermal conductivity meter test. The results are shown in table 3.

| Modified AlN (g) | 5.0  | 10.0 | 15.0  | 20.0 |
|------------------|------|------|-------|------|
| Thermal conductivity [W/(m·K)] | 0.2937 | 0.2976 | 0.4267 | 0.5941 |

In order to observe the effect on the thermal conductivity of the potting compound with different AlN powder’s addition. More intuitively, the analysis results are shown in figure 3.

Figure 3. Thermal conductivity of the potting compounds under different mass of modified AlN.

It can be found that the law of changes of the thermal conductivity of the potting compound under different mass of modified AlN powder according to table 3 and figure 3. The thermal conductivity of the potting compound was even less than 0.3W/(m·K) in the case of little amount of modified AlN powder added. However, it is thermal conductivity increased rapidly as the mass of modified AlN powder increasing. The increase of thermal conductivity of the potting compound was more obvious when the mass of modified AlN over 15.0 g. The thermal conductivity was as high as 0.5941 W/(m·K) when the mass of the modified aluminum nitride powder reaches 20.0 g. This was because the aluminum nitride powder must first form a heat conduction network in order to achieve heat
conduction in the potting compound which was equivalent to connecting the isolated islands in the sea. The thermal conduction points are isolated from each other when the mass of modified AlN powder is low. A good thermal conduction network was formed and thermal conduction channels were increased with the increase of the mass of addition. This also proved the excellent thermal conductivity of aluminum nitride.

3.3. Mechanical Properties Analysis
The sample was placed in an electronic universal testing machine for tensile property testing. The stress-strain curve obtained according to the test results. They are shown in figure 4.

![Stress-strain curves of the potting compound under different mass of modified AlN.](image)

**Figure 4.** Stress-strain curves of the potting compound under different mass of modified AlN.

From the stress-strain curves of the potting compound under different mass of AlN in figure 4 that the tensile strength information of the potting compound can be obtained.

**Table 4.** Tensile strength of the potting compound under different mass of modified AlN.

| Modified AlN (g) | 5.0   | 10.0  | 15.0  | 20.0  |
|-----------------|-------|-------|-------|-------|
| Tensile Strength $\sigma_M$ (Mpa) | 5.154 | 4.667 | 5.629 | 3.746 |

It can be found that the mechanical properties of the potting compound showed jagged changes with the mass of modified aluminum nitride increasing according to figure 4 and table 4. The maximum tensile strength of the potting compound became smaller when the mass of modified AlN increased from 5g to 10g. The maximum tensile strength of the potting compound became larger when the mass of modified AlN increased from 10g to 15g. And it got smaller again when the mass of modified AlN increased to 20g. The tensile strength of the potting compound was the largest when the mass of modified AlN was 15g and it was as high as 5.629MPa; The tensile strength of the potting compound was the smallest when the added amount was 20g with a value of 3.746MPa. It was because that the aluminum nitride powder only contributes greatly to the potting compound in terms of thermal conductivity but not so much to mechanical properties. Moreover, it may have made a certain impact on the trend of mechanical properties due to the formation of a thermal network. The resulting regularity was not so obvious.

3.4. Micromorphology (SEM)
The dispersibility of the nano-aluminum nitride powder in TPU was observed, and the results are shown in figure 5.
Figure 5. Micromorphology of the potting compound.

In figure 5, the mass of AlN added to a1 and a2 were 5 g, b1 and b2 were 10 g, c1 and c2 were 15 g, d1 and d2 were 20 g. By observing the micromorphology of the potting compound added with nano-aluminum nitride (AIN) powder, it can be found that the modified nano-aluminum nitride had a good
dispersibility in the matrix thermoplastic polyurethane (TPU). And no agglomeration was observed. It can be also found that the density of aluminum nitride (AlN) powder in TPU increasing as the mass fraction of nano-aluminum nitride (AlN) powder increasing at the same time. And the mechanism of heat conduction was a heat conduction network needs to be formed in advance, and the heat conduction network got more and more complete as the mass of modified AlN increasing, and the heat conduction channels increased too. It also further illustrated that the use of titanate coupling agent YB-201 to modify aluminum nitride powder was successful and the effect was obviously.

4. Conclusion
The modified nano-aluminum nitride (AlN) powder was added to polyurethane for the preparation of thermally conductive potting compound and the properties were tested and analyzed. The research results found that the conductivity of the potting compound increased slightly as the mass of nano-aluminum nitride (AlN) powder increased. However, the colloid was still in an insulating state. This phenomenon may be caused by the small size effect of nanomaterials and this effect caused little amount of electrons migration, so there was a tendency for the conductivity to increase slightly. This also provided a feasible way for improving the conductivity of materials; The thermal stability of the potting compound was getting more and more enhanced with the mass fraction of the aluminum nitride (AlN) powder increasing. The reason was that a thermal network must be formed firstly in order to achieve perfect thermal conductivity of the potting compound. Isolated thermally conductive points were connected to each other as the mass of aluminum nitride powder increasing, and a good thermal network was formed, and thermal channels were increased too. The high thermal conductivity of aluminum nitride was well demonstrated. Its mechanical properties showed a Jagged change without regularity with the mass of aluminum nitride increasing. In general, the dispersibility of modified nano aluminum nitride (AlN) powder in the matrix thermoplastic polyurethane (TPU) was perfect.

The polyurethane-based AlN potting compound studied in this article had excellent thermal conductivity and mechanical properties. The preparation process was simple. It could achieve a large-scale production in existing industrial production equipment. The required raw material sources were broadly and the economic cost was low. Polyurethane-based AlN potting compound will have broad market prospects in the future.

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