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Study on the Performances of Toughening UV-LED-Cured Epoxy Electronic Encapsulants

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Abstract: This study aims to investigate the effects of three toughening agents—core–shell rubber particles (CSR), nano-silica particles (NSPs), and epoxidized polybutadiene (EPB)—on the performance of UV-LED-cured epoxy electronic encapsulants. By systematically comparing the curing behavior, thermomechanical properties, and impact resistance of different toughening agents in alicyclic epoxy resins, their potential applications in more environmentally friendly UV-cured electronic encapsulation are evaluated. The results show that NSP and CSR toughened samples have fast cured speed under 365 nm UV-LED light, but it affects the depth of curing under low energy conditions. They maintain high Tg, high modulus, and low thermal expansion coefficient (CTE), especially in the NSP-toughened sample. The EPB-toughened sample has good transparency for LED, but it has negative effects on Tg and CTE. This research provides essential theoretical and experimental data to support the development of high-performance UV-LED-cured epoxy encapsulation materials.

Keywords: epoxy; cationic; UV curing; toughening; electronic encapsulation

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1. Introduction

Electronic encapsulation materials play a crucial role in the modern electronics industry, protecting electronic components from mechanical damage, chemical corrosion, and environmental influences. Epoxy resins are widely used in electronic encapsulation due to their excellent mechanical properties, adhesive performance, and chemical stability. However, traditional epoxy resin systems are often limited by their inherent brittleness and lack of toughness, which restrict their application in high-performance electronic devices [1–3]. In recent years, UV-LED curing technology has emerged as a promising approach in the field of electronic encapsulation due to its rapid curing, low-temperature processing, and environmentally friendly characteristics [4].

To address the brittleness of epoxy resins, toughening modification has been extensively studied. Common toughening agents include core–shell rubber particles (CSR), nano-silica particles (NSPs), and epoxidized polybutadiene (EPB). These toughening agents have demonstrated significant improvements in the toughness of thermally cured epoxy resins [5–10]. However, their effectiveness in UV-LED-cured epoxy systems requires further investigation. Understanding the behavior of these toughening agents in UV-LED-cured epoxy resins is essential for developing high-performance encapsulation materials.

Core–shell rubber particles consist of a rubbery core encapsulated by a hard shell. In thermally cured epoxy resins, CSR effectively absorbs stress and enhances impact strength by dissipating energy through the rubbery core [11–13]. In UV-LED-cured systems, the incorporation of CSR can improve the toughness and flexibility of the epoxy resin. The UV-LED curing process, with its rapid and low-temperature characteristics, may influence the dispersion and phase separation of CSR within the epoxy matrix. Therefore, it is crucial to investigate the behavior of CSR in UV-LED-cured systems to optimize their toughening efficiency.

Nano-silica particles are known for their high specific surface area and excellent interfacial reinforcement capabilities [14–16]. In thermally cured epoxy resins, NSP enhances mechanical properties and thermal stability by improving the resin's modulus and reducing the coefficient of thermal expansion [17–20]. In UV-LED-cured epoxy systems, NSP can provide similar benefits, but their dispersion and interaction with the epoxy matrix under UV-LED curing conditions must be thoroughly examined. The uniform distribution of NSP may affect UV-LED curing reactivity, impacting the overall material properties.

Epoxidized polybutadiene is a flexible polymer with good chemical compatibility with epoxy resins. In thermally cured systems, liquid rubber improves the toughness and elasticity of the epoxy resin by providing a flexible network structure. In UV-LED-cured systems, EPB's effectiveness as a toughening agent is influenced by the rapid curing process and low curing temperatures. EPB can enhance the flexibility and impact resistance of the UV-LED-cured epoxy resin, making it a suitable candidate for improving the toughness of electronic encapsulation materials [21–26].

UV curing technology has been used for over 50 years, primarily in industries like printing, coatings, and adhesives, where rapid curing times and efficient processing were needed [27,28]. Traditional UV curing systems typically utilize mercury vapor lamps as the light source, which emit a broad spectrum of UV light. However, these systems had several limitations, including high energy consumption, heat generation, a short lamp lifespan, and the use of toxic mercury. Over the past two decades, UV-LED curing has gained increasing attention in fields like printing, coatings, and adhesives and, more recently, in advanced electronic packaging [29,30]. Its ability to cure at lower temperatures without generating high levels of heat makes it ideal for applications where temperature-sensitive electronic devices need to be encapsulated without compromising their structural integrity.

Toughening UV-LED-cured epoxy resins is significant due to the unique advantages of UV-LED curing technology [31,32]. The rapid and low-temperature curing process of UV-LED curing enables the encapsulation of temperature-sensitive electronic components, reducing thermal stress and potential damage. Additionally, the environmentally friendly nature of UV-LED curing, with minimal volatile organic compound (VOC) emissions, aligns with the growing demand for sustainable manufacturing processes. By incorporating toughening agents such as CSR, NSP, and EPB, the mechanical performance, thermal stability, and impact resistance of UV-LED-cured epoxy encapsulants can be significantly improved, enhancing their reliability and durability in electronic applications [33].

The core theme of this study is the influence of different types of toughening agents on the toughness, thermomechanical properties, and curing behavior of UV-LED-cured epoxy resins. Through systematic experiments and analysis, this paper aims to clarify the role mechanisms of the three toughening agents in epoxy resins, providing theoretical support and experimental evidence for the development of high-performance UV-LED-cured epoxy encapsulation materials. The specific research objectives include (1) evaluating the effect of different toughening agents on the curing behavior of epoxy resins; (2) analyzing the improvement of thermomechanical properties of epoxy resins by toughening agents; and (3) exploring the impact of toughening agents on the adhesion and resistance to humid heat environments of epoxy resins. Through systematic experimental research and theoretical analysis, this paper aims to provide new ideas for the toughening modification of UV-LED-cured epoxy resins and promote the development of high-performance electronic encapsulation materials.

2. Materials and Methods

2.1. Experimental Reagents

The chemicals are as follows:

- One alicyclic epoxy resin as 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (EEC), CELLOXIDE 2021P, Daicel, Osaka, Japan;
- Triarylsulfonium hexafluoroantimonate salt (PAG), PAG20102, industrial grade, Qiangli Chemical, China;

- Core–shell rubber particles (CSR) with a core–shell rubber dispersion solution, MX553, Kaneka, Osaka, Japan;
- Nano-silica particles (NSPs) with a nano-silica dispersion solution, Nanopox E601, Evonik, Shanghai, China;
- and Epoxidized PolyButadiene (EPB), EPOLEAD PB3600, Daicel, Osaka, Japan.

Other materials are as follows:

- Spherical silica, FB35, Denka, Tokyo, Japan.

All chemicals were used without special treatment before use.

2.2. Sample Preparation

Under yellow light conditions, the experimental raw materials were mixed according to the formulation ratio in Table 1. First, EEC and PAG were mixed with a speed mixer (mixing speed 1000 rpm) until PAG was completely dissolved in the liquid. Then, NSP, CSR, and EPB were added and mixed by a speed mixer (mixing speed 1000 rpm, 3 mins), respectively. Finally, spherical silica was added as a filler and dispersed evenly. The samples were degassed in a speed mixer and sealed in a 30 cc syringe, then stored in −20 °C condition.

Table 1. Formulation of testing samples.

Formulations	**Blank**	**NSP (E601)**	**CSR (MX553)**	**EPB (PB3600)**
EEC	20	20	20	20
PAG	1	1	1	1
Spherical Silica *	30	30	30	30
NSP	0	5	0	0
CSR	0	0	5	0
EPB	0	0	0	5

* Not add spherical silica for SEM and TGA tests.

UV Curing Conditions: 365 nm UV-LED floodlight box, light intensity 100 mW/cm^2, UV dose: 3000 mJ/cm^2 and 5000 mJ/cm^2.

2.3. Experimental Testing and Characterization

Curing depth testing method: Epoxy adhesive packed by syringe is injected into a mold with a 2 mm diameter and 10 mm deep hole and cued in a 365 nm UV-LED floodlight box, light intensity 100 mW/cm^2, UV dose: 3000 mJ/cm^2 and 5000 mJ/cm^2. Take the samples out of the mold and measure the curing thickness of the solid adhesive with a vernier caliper.

Dynamic mechanical analysis (DMA) was conducted on a TA Q800 DMA apparatus (TA, New Castle, DE, USA) to analyze storage modulus and loss factor. Samples with dimensions of 50 mm × 6 mm × 2 mm were fixed on a tension clamp and tested in tensile mode from −50 °C to 250 °C with a heating rate of 5 °C/min at a frequency of 1.0 Hz.

Thermomechanical analysis (TMA) was performed on a TA Q400 TMA (TA, New Castle, DE, USA) to analyze the coefficient of thermal expansion (CTE) and the glass transition temperature (Tg). The samples were heated from −50 °C to 250 °C at a heating rate of 5 °C/min.

Thermogravimetric analysis (TGA) curves were obtained on a TA Q55 TGA (TA, New Castle, DE, USA) under an air atmosphere to analyze thermal weight loss performance.

The UV-DSC method was tested by a TA Q100 DSC instrument (TA, New Castle, DE, USA) equipped with an S2000 UV curing accessory (365 nm LED) at a light intensity of 200 mW/cm^2.

Scanning electron microscopy (SEM) was measured on a Hitachi S3600 to observe fractured surfaces. Samples were frozen in liquid nitrogen and then fractured. Fractured surfaces were coated with a thin layer of platinum before observation.

Three point bending tests were recorded by an Instron universal material testing machine with a test speed of 2 mm/min according to the GB/T 7124-2008 standard [34]. At least five samples were tested for each group.

Die shear strength (DSS) tests on the DAGE 4000 test equipment of the Nordson company (Carlsbad, CA, USA) were used to measure the adhesion ability of UV epoxy adhesive. Under yellow light conditions, the glass chip and the FR4 substrate are bonded by uncured epoxy adhesive and fully cured in a 365 nm LED light box according to the designed curing conditions. Under the temperature condition of 25 °C, the test speed is 200 µm/s, and the height of the test cutter head from the substrate is 35 µm, and the shear strength is tested. A total of 10 samples were tested repeatedly in each experimental group, and the average value was taken.

3. Results and Discussion

3.1. UV-DSC Analysis

The curing behavior of UV-LED-cured epoxy adhesives with different toughening agents was studied using UV-DSC. The exothermic peak represents the curing reaction, and the area under the curve corresponds to the degree of curing. Figure 1 shows the DSC curves of different formulations.

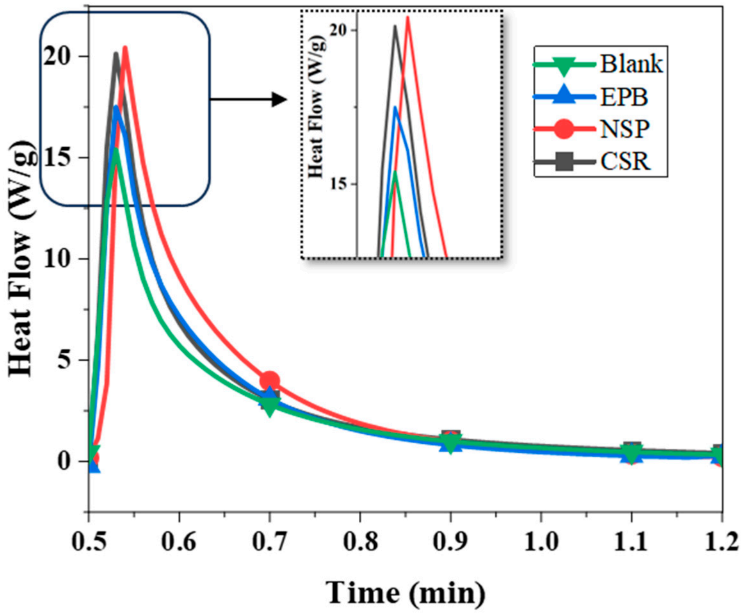

Figure 1. UV-DSC curves of different toughening epoxy formulations.

From Figure 1 and Table 2, the blank sample (without toughening agents) exhibited a sharp exothermic peak, indicating a fast-curing reaction. The addition of EPB slightly broadened the exothermic peak, suggesting a slight reduction in curing speed due to the increased viscosity and dispersion of the rubbers. However, there are more epoxy groups than blank samples, and it showed a higher peak than blank samples. NSP resulted in the broadest and most delayed exothermic peak, indicating the most significant hindrance to the curing reaction. However, it showed a higher peak than blank samples and EPB samples because NSP dispersed in epoxy resin. When adding NSP to the formulation, more epoxy resins are added than blank sample. Core–shell rubber particles (CSR) also broadened the exothermic peak. The rubber phase can absorb UV energy and hinder the curing process. It also showed a high peak close to NSP. Pramanik M [35] showed CSR has -COOH groups on the shell, which can accelerate the reactivity. That also resulted in a higher exothermic peak. Baek, D [36] observed that the CSR content delayed the reaction rate in the range of 1.8–2.5 min on the basis of the peak of heat flow. Table 1 also shows the exothermic energy. The NSP sample has the highest exothermic energy, so it has the highest reactivity. The CSR sample is very close to the NSP sample and also has high reactivity. EPB sample has lower exothermic energy than NSP and CSR sample, but it is still higher than blank sample. So, all the tougheners increased the reactivity of the epoxy system. Despite the variations in curing kinetics, all formulations achieved a high degree of curing, essential for ensuring the final material properties.

Table 2. Heat flow peak and exothermic energy in UV-DSC.

Formulations	Heat Flow Peak (W/g)	Exothermic Energy (J/g)
Blank	15.16	117.2
NSP	20.43	144.0
CSR	20.23	140.2
EPB	17.94	123.0

3.2. UV Curing Depth

The curing depth is a critical parameter for UV-cured materials, especially in electronic encapsulation, where complete curing throughout the material thickness is necessary. Figure 2 illustrates the curing depth of different formulations.

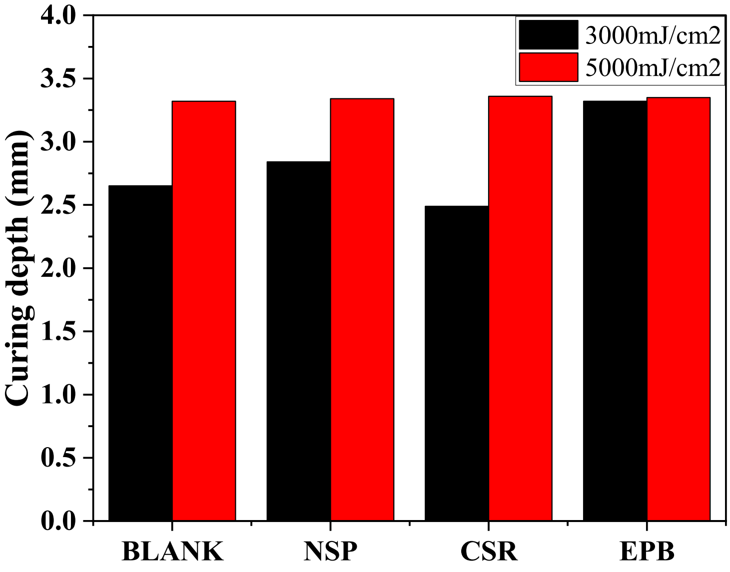

Figure 2. UV curing depth under 365 nm UV-LED.

From the chart, under low curing energy (3000 mJ/cm^2), EPB samples showed the deepest curing depth, consistent with its rapid curing reaction, even much deeper than the blank samples. NSP slightly reduced the curing depth, likely due to the increased scattering of UV light by nanoparticles. CSR further reduced the curing depth, with the rubber phase absorbing more UV light and limiting penetration, even though it was shallower than the blank samples. CSR had the most significant impact from the shell and core rubber, resulting in the shallowest curing depth due to its opacification and UV light absorption. After increasing the curing energy to 5000 mJ/cm^2, the curing depth showed different results compared to low curing energy. When the samples were cured with 5000 mJ/cm^2 UV energy, all the samples had similar curing depths.

Under enough curing energy conditions, the influence of tougheners can almost be ignored. Overall, while toughening agents affect the curing depth, the formulations and application process were adjusted to ensure sufficient curing for practical applications. But EPB is a better toughener for low-energy curing conditions.

3.3. Thermal Properties of UV Epoxy Adhesive Modified by Different Tougheners

3.3.1. Dynamic Mechanical Analysis (DMA)

DMA was used to evaluate the thermomechanical properties of the cured formulations. Figure 3a,b present the storage modulus and loss factor (tan δ) curves, respectively. The blank sample exhibited the highest storage modulus, indicating the highest rigidity. The addition of NSP improved the storage modulus compared to CSR and EPB due to the reinforcing effect of the nanoparticles. CSR showed a moderate decrease in storage modulus, with the rubber phase providing some flexibility. EPB resulted in the lowest storage modulus, reflecting its significant toughening effect at the expense of rigidity.

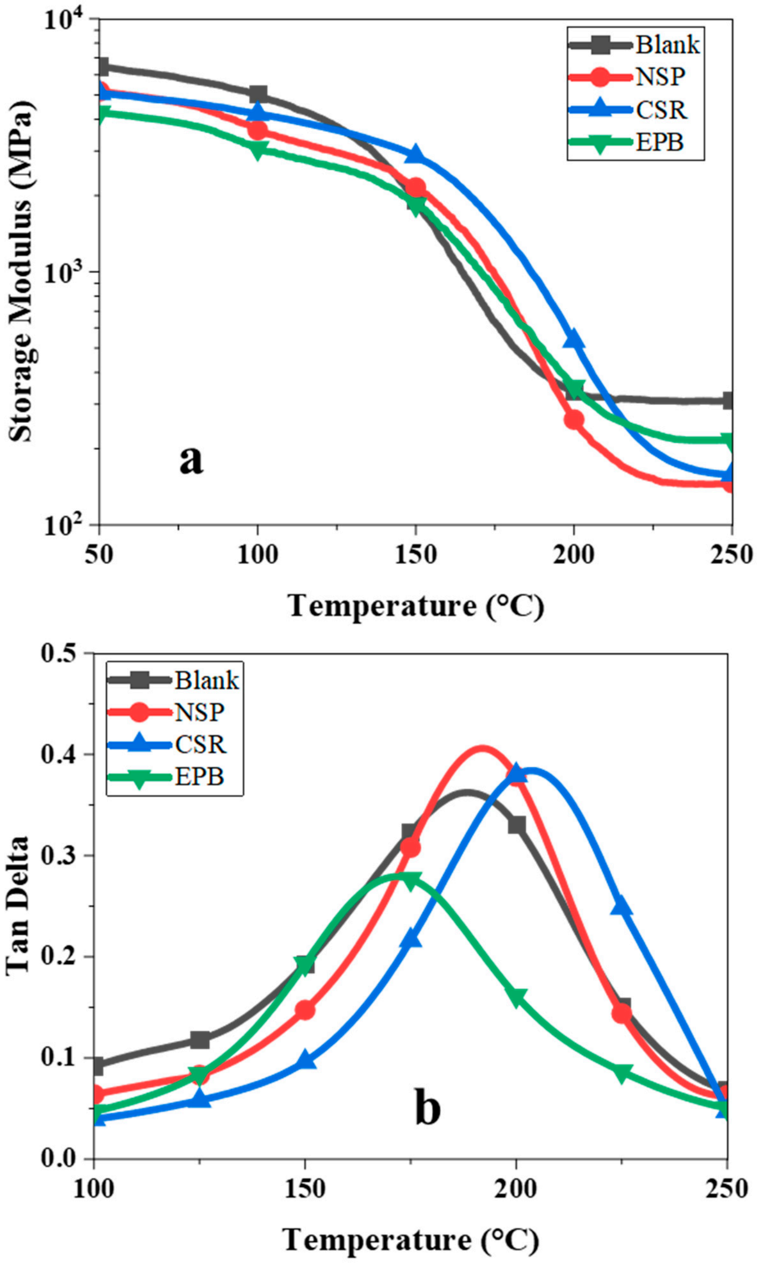

Figure 3. DMA test result. (**a**) Storage modulus; (**b**) loss factor.

The tan delta peak represents the glass transition temperature (Tg). NSP and CSR toughening agents shifted the Tg to higher temperatures, but EPB shifted to a lower direction. EPB toughened adhesive has the most pronounced effect due to EPB flexible polymer chains with low Tg. Baek, D [36] also found that more CSR content in epoxy adhesive, Tg, shifted to a higher temperature. So, CSR can improve the epoxy sample Tg in both the thermal system and the UV curing system, even if the epoxy resin is different and the curing condition is different.

3.3.2. Thermomechanical Analysis (TMA)

The thermal expansion behavior was analyzed by TMA. Figure 4 shows the thermal expansion curves. The blank sample exhibited the lowest thermal expansion coefficient (CTE), indicative of its inherent brittleness. NSP samples also had the lowest CET below Tg and reduced the CTE above Tg, improving thermal stability due to the stiffening effect of the nanoparticles. CSR moderately increased the CTE with the rubber phase balancing flexibility and thermal stability. EPB showed the highest CTE, demonstrating its worse effectiveness in enhancing thermal stability and reducing expansion because of its soft chains. Table 3 also shows the Tg of each sample. NSP has the highest Tg, and the following is CSR. Both of the tougheners have a higher Tg than the blank sample. But EPB has a lower Tg than a blank sample. The result is the same with DMA results. NSP also showed the lowest CTE below Tg and above Tg. The CTE of CSR and EPB is a little higher than the blank sample because of its soft rubber phase.

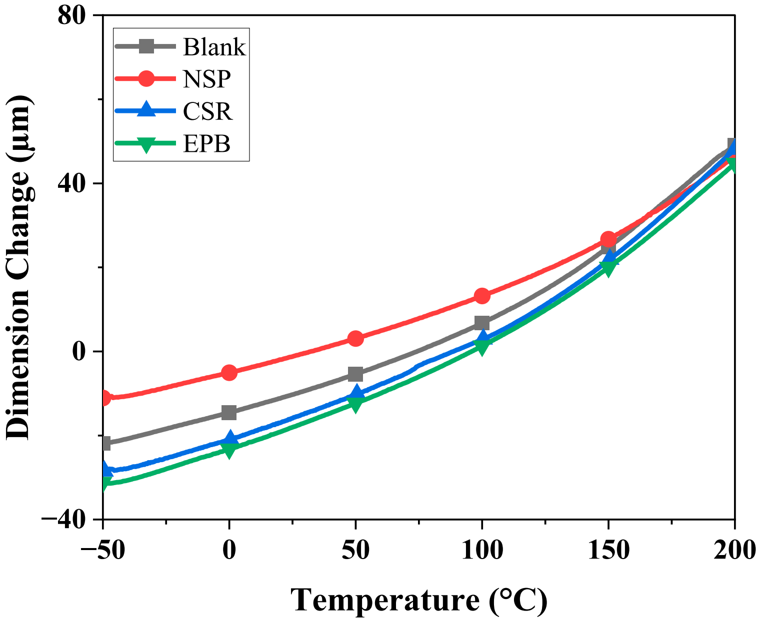

Figure 4. Dimension change curve tested by TMA.

Table 3. CTE and Tg by TMA.

Formulations	CTE Below Tg (μm/(m·°C))	CTE Above Tg (μm/(m·°C))	Tg (°C)
Blank	27	84	113
NSP	27	73	130
CSR	32	92	120
EPB	33	84	107

3.3.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of the cured epoxy formulations with different toughening agents. TGA measures the weight loss of a material as a function of temperature, providing insights into its thermal decomposition behaviors. Figure 5a,b showed the TGA curves of the various formulations. All the samples exhibited a two-step decomposition process. The initial weight loss occurred around 300 °C, corresponding to the degradation of the epoxy resin matrix. The second major weight loss occurred around 450 °C, indicating the breakdown of the remaining polymer structure.

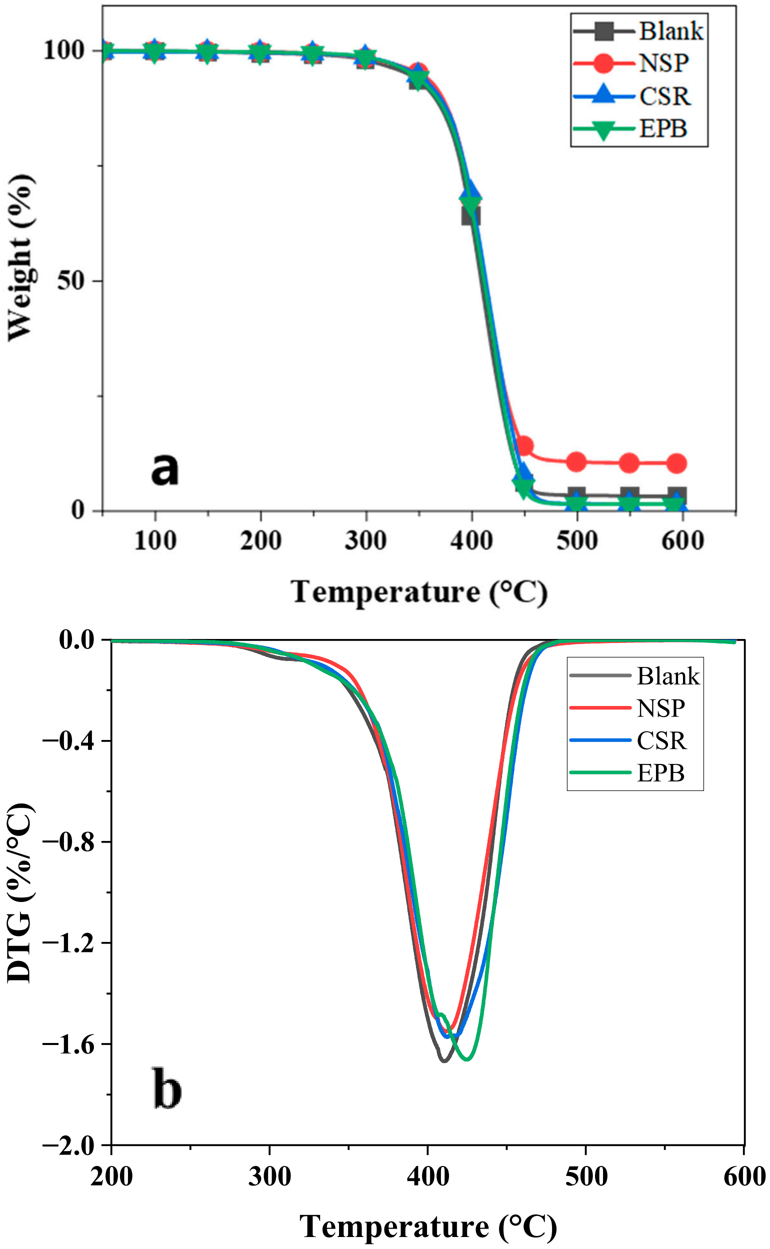

Figure 5. TGA test result. (**a**) TGA thermograms; (**b**) derivative of TGA curves by temperature.

Table 4 shows the details of the TGA properties of these formulations. The blank sample showed 2.0% weight loss at 300 °C and 5% weight loss at 339.5 °C, which is the lowest temperature of all the samples. The NSP-enhanced formulation showed improved thermal stability compared to the blank sample. A total of 5% weight loss was delayed at 351.3 °C, just 1.5% weight loss around 300 °C. The presence of nano-silica particles enhances thermal stability by acting as a barrier to thermal degradation. The CSR formulation exhibited a similar decomposition profile to the NSP sample but with slightly higher thermal stability than the blank sample. The initial weight loss was observed around 310 °C. The rubber phase contributes to a more gradual weight loss, indicating improved thermal stability. The EPB formulation displayed the highest thermal stability among the tested samples. The 5% weight loss temperature showed around 346.2 °C, and the weight loss at 300 °C was lower compared to the other formulations. The flexible polymer chains of EPB enhance the thermal stability by improving the thermal degradation resistance.

Table 4. Thermogravimetric properties of toughened epoxy systems.

Formulations	$T_{5\%}$ (°C)	Weight Loss at 300 °C (%)	Residual Weight (%)
Blank	339.5	2.0	3.3
NSP	351.3	1.5	10.4
CSR	347.2	1.4	1.5
EPB	346.2	1.2	1.4

The residual weight at different temperatures provides additional information about the thermal stability and the amount of non-volatile components in the formulation. Table 4 summarized the residual weight percentages at 500 °C for each formulation.

The blank sample had a moderate residual weight of 3.3%, indicating that most of the materials decomposed after 500 °C. The NSP formulation had the highest residual weight due to nano-silica being an inorganic material, reflecting the thermal stability imparted by the nano-silica particles. The CSR and EPB formulations showed the lowest residual weight, balancing the rubber phase's contribution to thermal stability.

The TGA analysis revealed that the inclusion of different toughening agents significantly impacts the thermal stability of UV-LED-cured epoxy formulations. Nano-silica particles (NSPs) and epoxidized polybutadiene (EPB) notably enhance thermal stability, with EPB showing the highest overall improvement. Core–shell rubber particles (CSR) also contribute to improved thermal stability due to their special shell and core structure. These findings underscore the importance of selecting appropriate toughening agents to enhance the thermal performance of UV-LED-cured epoxy encapsulants, providing a basis for developing materials with optimized properties for electronic applications.

This comprehensive analysis of the TGA results further supports the experimental findings, offering valuable insights into the thermal behavior of UV-LED-cured epoxy formulations with different toughening agents.

3.4. Mechanical Properties and Fractured Surfaces of UV Epoxy Adhesive Modified by Different Tougheners

Compressive resistance was assessed to evaluate the toughness of the formulations by three-point bending. Table 5 summarizes the compressive strength results. The blank sample had the highest strength, reflecting its brittleness. NSP significantly reduced the compressive stress due to the toughening effect of the nanoparticles. The EPB sample showed the lowest compressive stress, with the rubber phase effectively absorbing impact energy. The CSR sample also decreased the compressive stress, but to a higher extent than EPB, balancing toughness and flexibility.

Table 5. Average values of compressive stress and load strength.

Formulations	Compressive Stress (MPa)	Load (N)
Blank	127	212
NSP	120	201
CSR	116	194
EPB	97	161

The effect of different tougheners on the impact cross-section morphology of a cationic UV-cured epoxy system is shown in Figure 6. Compared to the pure epoxy system fracture surface (Figure 6(a1,a2)) with a relatively smooth cross-section and uniform silver lines, it was found that the fracture surface of the CSR particle-modified epoxy system is much rougher, as shown in Figure 6c. The crack surface is covered with many voids, which can be recognized as circular features. For CSR particles, the generation of voids may be caused by three mechanisms: CSR shell and substrate debonding, CSR rubber core cavitation, and CSR core and CSR shell debonding. Further research was conducted on the initiation mechanism of these gaps. The coarseness of the interface curve formed by the addition of

NSP material is significantly increased, as shown in Figure 6b. The increase in irregular grooves in the irregular cross-section indicates that a large amount of impact energy is absorbed during the formation process of the cross-section. During the silver line growth process, the obstruction of the silver lines is encountered, and some stress is transferred from the resin matrix layer to the nano-silica particles. This process consumes a large amount of external energy, thus improving the initial properties of the system. Compared with the cross-section of the NSP formulation, the significantly rougher surface was shown in Figure 6d after adding EPB. The cross-sectional morphology analysis provides good evidence of the cleverness of modified epoxy resin with tougheners.

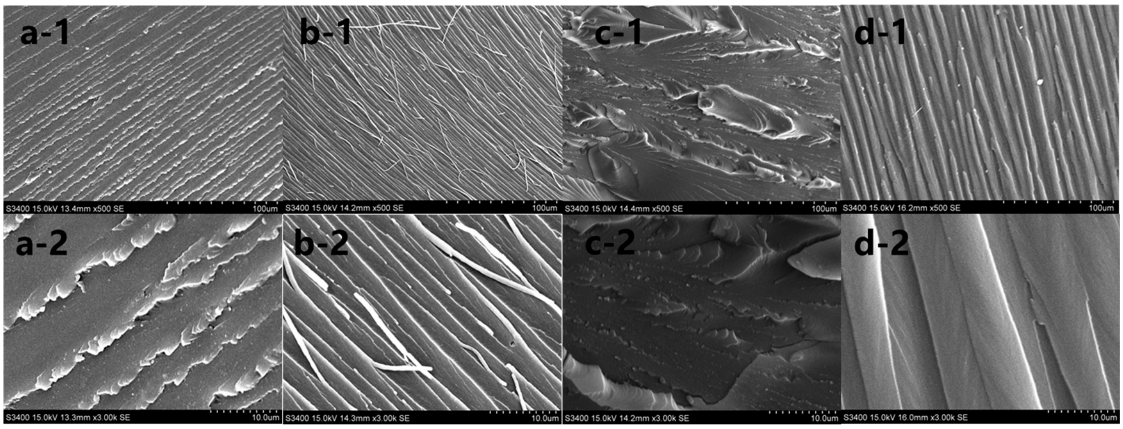

Figure 6. SEM images of fractured sections of (**a**) Blank, (**b**) NSP, (**c**) CSR, and (**d**) EPB. a-1, b-1, c-1 and d-1 pictures are under 500SE, a-2, b-2, c-2 and d-2 pictures are under 3000SE.

3.5. Chiplet Adhesion (DSS)

The die shear strength of the glass chip bonded with an epoxy adhesive was tested with a DAGE thrust testing machine, and the bonding strength of the epoxy adhesives was evaluated by this thrust. The adhesion of each toughened system to the chiplet (3 × 3 mm) at room temperature (25 °C) was tested separately, as shown in Figure 7. Under the test conditions at room temperature, with the addition of toughener, the shear strength of the epoxy adhesive to the glass chip decreases slightly, but it can basically maintain a strong adhesion range of 300–350 N. The addition of tougheners will cause the cohesion of the epoxy adhesive itself to have a certain effect, which leads to a slight decrease in the bonding shear strength of the chip.

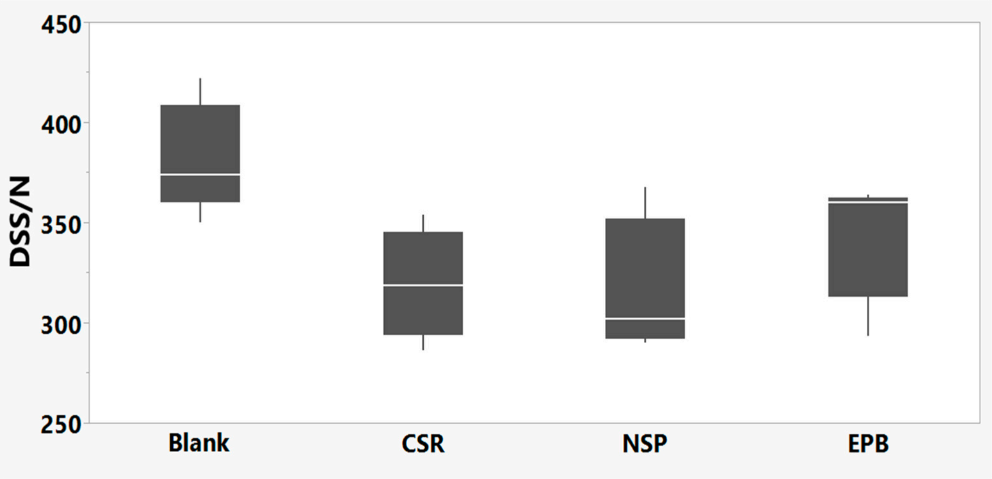

Figure 7. Die shear strength (DSS) test result.

3.6. Water Absorption

High-performance electronic packaging materials require high moisture resistance, and improving moisture resistance is of great significance in protecting packaging devices from external environmental influences and extending their lifespan. The water absorption rate is an important parameter to characterize moisture resistance. The smaller the water absorption rate, the better the moisture resistance. The effect of different tougheners on the water absorption of the cationic UV-cured epoxy system is shown in Figure 8. The test condition is in an 85 °C and 85% humidity oven box for 72 h.

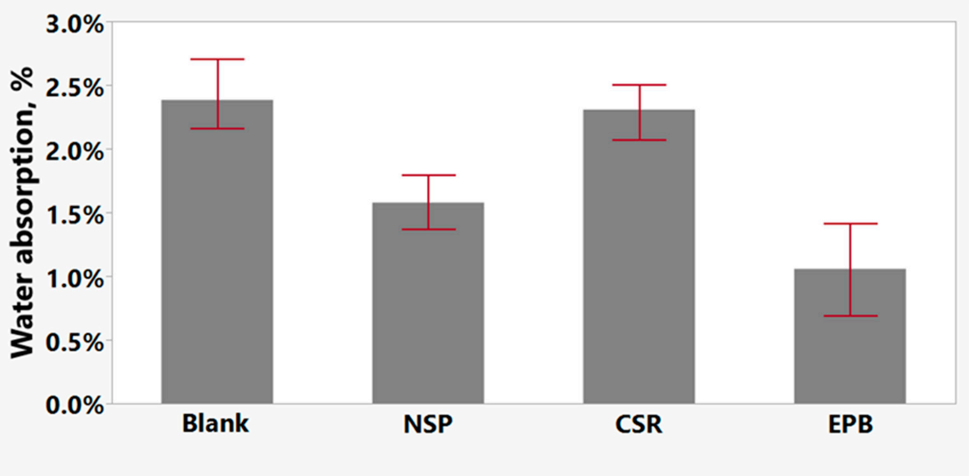

Figure 8. Water absorption after 72 h in 85 °C and 85% humidity oven box 72 h testing.

From Figure 8, different tougheners have different effects on the water absorption of this UV-cured epoxy system. Compared to pure epoxy systems, NSP and EPB systems have lower water absorption, especially EPB systems. After participating in epoxy resin crosslinking and curing in a cationic UV system, the crosslinking density is reduced, resulting in an increase in free volume and a decrease in the system's moisture resistance. In addition, EPB is rich in hydrophobic C-H bonds, which form a homogeneous structure with epoxy resin during the curing process, which can improve moisture resistance. The interaction between the two results in almost no change in the water absorption rate of the system.

4. Conclusions

This study found that the addition of toughening agents such as CSR, NSP, and EPB significantly improved the toughness and thermal stability of UV-cured epoxy resins. Among them, the samples toughened with NSP and CSR have fast cured speed under 365 nm UV-LED light, but it affects the depth of curing under low energy conditions. At the same time, in terms of thermomechanical properties, the samples toughened with NSP and CSR always maintain high Tg, high modulus, and low thermal expansion coefficient (CTE). The addition of EPB has little effect on the transmittance of light, which is conducive to deeper curing under low energy. However, EPB will reduce the Tg and storage modulus of the sample after curing. After toughening, the bonding strength of the chips is slightly reduced compared to the pure epoxy system. The improvement mechanisms and impact of each toughening agent were distinct, providing a robust foundation for the development of high-performance electronic encapsulation materials. Future research can further explore different types of nano-toughening agents to understand their interaction mechanisms with UV-curable systems, contributing to the development of high-performance, multifunctional UV-curable materials.

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