



## **Role of Epoxy Ring Functionality on the Structural and Surface Properties of Epoxy-Based Coatings**

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## Abstract

Epoxy-based coatings are widely used in various protective applications due to their excellent adhesion, chemical stability, and mechanical performance. The epoxy ring is a key functional group that governs crosslinking reactions and interfacial interactions within these coatings. In this study, the role of epoxy ring functionality on the structural and surface properties of epoxy-based coatings was systematically investigated. Silica nanoparticles were surface-modified using an epoxy-functional silane coupling agent in order to introduce reactive epoxy groups at the organic–inorganic interface. The modified nanoparticles were then incorporated into an epoxy coating matrix. The resulting coatings were characterized in terms of chemical structure, thermal stability, surface morphology, and wettability. Fourier transform infrared spectroscopy (FTIR) was used to evaluate the presence and possible ring-opening behavior of epoxy groups, while thermogravimetric analysis (TGA) was employed to assess the thermal behavior and organic content of the coatings. Surface wettability was further analyzed through contact angle measurements. The results demonstrate that epoxy ring functionality plays a critical role in enhancing interfacial compatibility, improving nanoparticle dispersion, and tailoring the surface properties of epoxy-based coatings.

**Keywords:** Silica nanoparticles, GPTMS, surface modification, hydrophobic coating, epoxy ring, sol–gel, functionalization



## **1.Introduction**

Epoxy-based coatings are among the most widely used coating systems in industrial and engineering applications due to their excellent adhesion to various substrates, good chemical resistance, and favorable mechanical properties [1,2]. These coatings are commonly employed in protective, decorative, and functional applications where durability and surface performance are of primary importance.

The performance of epoxy coatings is strongly dependent on their molecular structure, particularly the presence and reactivity of epoxy rings. Epoxy rings are highly reactive functional groups that can undergo ring-opening reactions with nucleophilic species such as amines, hydroxyl groups, and carboxylic acids, leading to the formation of a crosslinked polymer network [3]. The extent of epoxy ring participation in these reactions directly influences the final structure, cohesion, and surface characteristics of the coating.

In recent years, the incorporation of inorganic fillers and nanoparticles into epoxy matrices has been extensively investigated as a strategy to improve coating properties such as thermal stability, mechanical strength, and surface behavior [4]. Among various inorganic fillers, silica nanoparticles have attracted significant attention due to their high surface area, chemical stability, and tunable surface chemistry. However, the intrinsic hydrophilicity of silica nanoparticles and their strong tendency to agglomerate often result in poor dispersion and weak interfacial interactions within epoxy matrices [5].

Surface modification of silica nanoparticles using silane coupling agents has been widely adopted to address these challenges. Epoxy-functional silanes, such as glycidyloxypropyl-based silanes, are of particular interest because they introduce epoxy rings at the organic–inorganic interface, enabling chemical interactions between the silica surface and the epoxy matrix [6,7]. The epoxy rings present on the modified nanoparticle surface can participate in curing reactions or interact with the surrounding polymer chains, thereby enhancing interfacial compatibility and dispersion quality.

Despite the widespread use of epoxy-functional silanes, the specific role of epoxy ring functionality—especially its presence, stability, and possible ring-opening behavior—on the structural and surface properties of epoxy-based coatings has not yet been fully elucidated. Most previous studies have focused on overall coating performance, while the fundamental contribution of epoxy ring chemistry to surface characteristics such as morphology and wettability remains insufficiently explored [8,9].

Therefore, the objective of this study is to systematically investigate the role of epoxy ring functionality on the structural and surface properties of epoxy-based coatings. By focusing on epoxy-functional interactions at the molecular and interfacial levels, this work aims to provide

deeper insight into the design of advanced epoxy coating systems with tailored surface characteristics.

## INtroduction

## 2. Materials and Methods

### 2.1. Materials

Epoxy resin was used as the coating matrix in this study. Commercial silica nanoparticles with an average particle size in the nanometer range were selected as the inorganic phase. An epoxy-functional silane coupling agent, 3-glycidyloxypropyltrimethoxysilane (GPTMS), was employed for surface modification of silica nanoparticles to introduce epoxy rings at the organic–inorganic interface. Ethanol and deionized water were used as solvents during the surface modification process. All chemicals were used as received without further purification.

### 2.2. Surface Modification of Silica Nanoparticles

Silica nanoparticles were surface-modified using GPTMS through a sol–gel based silanization process. Initially, a specific amount of GPTMS was dissolved in an ethanol–water mixture under magnetic stirring. The pH of the solution was adjusted to promote hydrolysis of the silane alkoxy groups. Subsequently, silica nanoparticles were gradually added to the solution and dispersed under continuous stirring for a fixed duration to allow silane hydrolysis and condensation reactions to occur on the nanoparticle surface. The modified nanoparticles were then separated, washed to remove unreacted silane molecules, and dried prior to incorporation into the epoxy matrix.

Table 1: Composition of nanoparticle coating

GPTMS (g)	Silica Nanoparticles (g)	Ethanol (mL)	Distilled Water (mL)	Solution pH	Magnetic Stirrer Temperature (°C)	Stirring Time (min)	Oven Temperature (°C)	Oven Drying Time (min)	Sample Code
0.5	1	100	-	7	60	160	55	300	CNPS0.5
1.5	1	100	-	7	60	160	55	300	CNPS1.5
2.5	1	100	-	7	60	160	55	300	CNPS2.5
3.5	1	100	-	7	60	160	55	300	CNPS3.5
0.5	1	70	30	3.5	60	450	60	480	ONPS0.5
1.5	1	70	30	3.5	60	450	60	480	ONPS1.5
2.5	1	70	30	3.5	60	450	60	480	ONPS2.5
3.5	1	70	30	3.5	60	450	60	480	ONPS3.5

### **2.3. Preparation of Epoxy-Based Coatings**

The surface-modified silica nanoparticles were incorporated into the epoxy resin at a predetermined weight percentage. The mixture was mechanically stirred to achieve homogeneous dispersion of nanoparticles within the epoxy matrix. The resulting coating formulation was applied onto suitable substrates using a conventional coating technique. The coated samples were then cured under controlled conditions to ensure completion of epoxy ring reactions and formation of a crosslinked network.

### **2.4. Characterization Techniques**

Fourier transform infrared spectroscopy (FTIR) was employed to investigate the chemical structure of the coatings and to evaluate the presence and possible ring-opening behavior of epoxy groups. Thermogravimetric analysis (TGA) was conducted to assess the thermal stability and organic content of the epoxy-based coatings. Surface morphology was examined using appropriate microscopic techniques. Surface wettability was evaluated by static water contact angle measurements, which were used as an indicator of surface property modification resulting from epoxy ring functionality.

## **3. Results and Discussion**

### **3.1. FTIR Analysis and Role of Epoxy Ring Functionality**

Fourier transform infrared spectroscopy (FTIR) was used to investigate the chemical structure of the epoxy-based coatings and to evaluate the presence and behavior of epoxy rings. The characteristic absorption band of the epoxy ring was observed in the range of  $910\text{--}920\text{ cm}^{-1}$ , which is commonly attributed to the asymmetric stretching vibration of the epoxy group. After incorporation of epoxy-functional silane-modified silica nanoparticles into the epoxy matrix, a noticeable change in the intensity of this band was detected. This observation suggests partial participation of epoxy rings in ring-opening reactions during the curing process or through interfacial interactions with surface hydroxyl groups on silica nanoparticles.

In addition, the appearance and/or enhancement of absorption bands corresponding to hydroxyl groups in the range of  $3200\text{--}3600\text{ cm}^{-1}$  further supports the occurrence of epoxy ring-opening reactions. These results indicate that epoxy ring functionality plays a significant role in establishing chemical linkages at the organic–inorganic interface, thereby contributing to improved structural integrity of the coating.

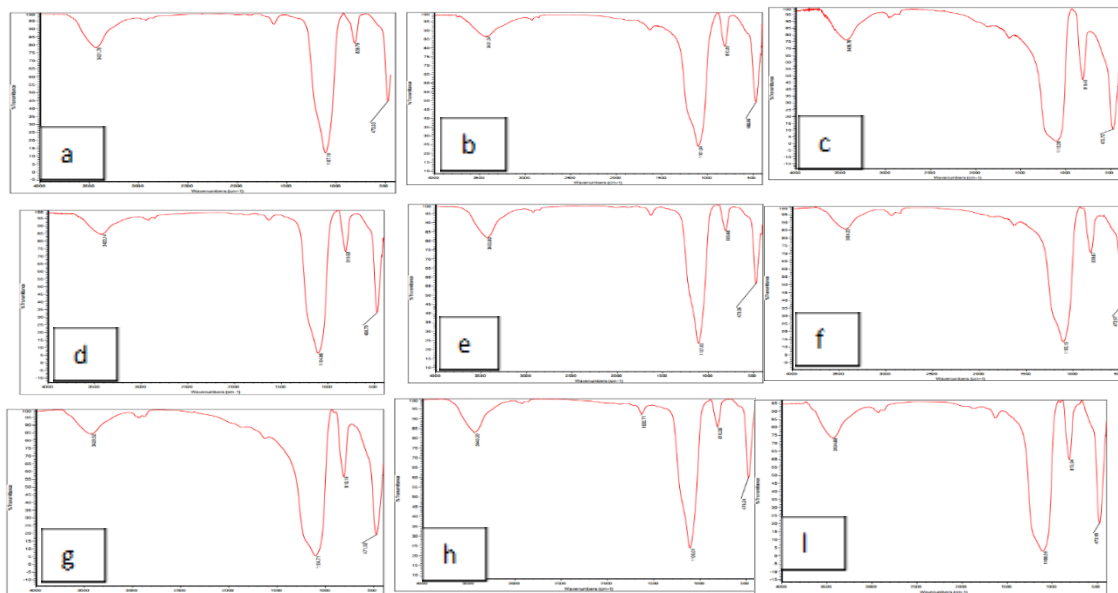


Figure 1: FTIR spectra of silica nanoparticles coated with GPTMS modifier: a) sample CNPS0, b) sample CNPS0.5, c) sample CNPS1.5, d) sample CNPS2.5, e) sample CNPS3.5, f) sample ONPS0.5, g) sample ONPS1.5, h) sample ONPS2.5, i) sample ONPS3.5

Table 2: Significant FTIR peaks of the samples

Observed peaks (cm <sup>-1</sup> )										Assignments
Nano-SiO <sub>2</sub>	GPTMS	CNPs 0.5	CNPS 1.5	CNPS 2.5	CNPS3 .5	ONPS 0.5	ONPS1 .5	ONPS2 .5	ONPS 3.5	
3431	~3400	3433	3426	3435	3435	3427	3440	3430	3440	O-H stretching vibration (hydroxyl/water)
-	~3048	-	-	3048	3048	3048	3048	3048	3048	C-H stretching vibration in Epoxy in GPTMS
-	~2960	2929	2929	2942	2942	2940	2942	2941	2942	Asymmetric C-H stretching vibration in CH <sub>2</sub> and CH <sub>3</sub> in GPTMS
-	~2850	2865	2865	2865	2842	2873	2841	2842	2841	symmetric C-H stretching vibration in CH <sub>2</sub> and CH <sub>3</sub> in GPTMS
1631	~1631	1631	1631	1631	1631	1631	1631	1631	1631	O-H bending vibration mode of absorbed water molecules
-	~1230	-	-	1207	1207	1207	1207	1207	1207	Asymmetric stretching of Epoxy ring in GPTMS
1105	~1110	1104	1100	1099	1090	1097	1090	1100	1097	Si-O-Si asymmetric stretching vibration/Si-O-C stretching vibration
-	~910	908	908	908	909	908	909	909	909	symmetric stretching of Epoxy ring in GPTMS
811	~800	809	808	813	815	807	817	817	818	Si-O-Si symmetric stretching vibration/ Epoxy ring bending
470	~470	473	470	470	472	468	470	467	472	Si-O-Si bending vibration

### 3.2. Thermal Behavior of Epoxy-Based Coatings

Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability and organic content of the prepared coatings. The TGA curves revealed a multi-step degradation behavior typical of epoxy-based systems. Coatings containing epoxy-functional silica nanoparticles exhibited a slight shift of the main degradation stage toward higher temperatures compared to the neat epoxy coating. This improvement in thermal stability can be attributed to enhanced interfacial interactions facilitated by epoxy ring functionality, which restricts polymer chain mobility and delays thermal decomposition.

Table 3: Weight loss of samples in TGA test

Description	300-400	400-500	500-600	Sample Number
The uncoated surface contains only adsorbed and surface moisture, which evaporates at low temperatures, and shows no significant weight loss at higher temperatures.	Negligible loss	Negligible loss	1%	NPS 0
The presence of GPTMS groups allows surface and adsorbed moisture to evaporate at low temperatures; silane organic groups decompose between 100–300 °C, and further decomposition of the organic and carbon network occurs above 300 °C.	5%	3%	2%	CNPS 3.5
In acidic environments, GPTMS undergoes hydrolysis and condensation, resulting in a higher fraction of organic groups being decomposed and degraded.	6%	4%	2%	ONPS 3.5

Furthermore, the residual mass at elevated temperatures was higher for nanocomposite coatings, indicating the presence of inorganic silica and the formation of a more thermally stable hybrid structure. These findings confirm the positive contribution of epoxy ring-mediated interactions to the thermal performance of the coating system.

Table 4: Zeta potential of the samples

Sample Number	NPS0	CNPS0.5	CNPS1.5	CNPS2.5	CNPS3.5	ONPS0.5	ONPS1.5	ONPS2.5	ONPS3.5
Zeta Potential (mV)	-1.1	-0.7	-0.751	-1	-0.8	0.3	0.1	0.1	0
Electrical Conductivity (mS/cm)	0.12	0.064	0.062	0.06	0.064	0.06	0.065	0.6	0.06

### 3.3. Surface Morphology and Nanoparticle Dispersion

Surface morphology observations demonstrated that the incorporation of epoxy-functional silica nanoparticles resulted in a more uniform and homogeneous surface compared to coatings containing unmodified nanoparticles. The improved dispersion behavior can be directly linked to the presence of epoxy rings on the nanoparticle surface, which enhances compatibility with the epoxy matrix through chemical and physical interactions. Reduced agglomeration of nanoparticles leads to a smoother surface morphology and minimizes the formation of micro-scale defects. This structural uniformity is crucial for achieving consistent surface properties and overall coating performance.

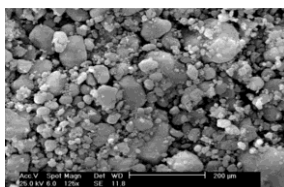


Figure 1: SEM image of the raw nanoparticles.

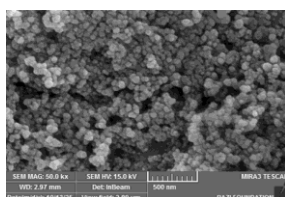


Figure 3: SEM image of CNPS3.5 nanoparticles

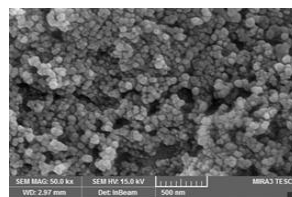


Figure 4: SEM image of CNPS0.5 nanoparticles.

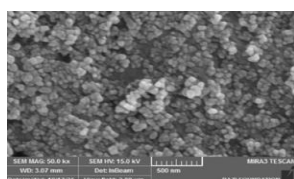


Figure 5: SEM image of ONPS3.5 nanoparticles.

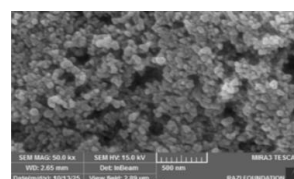


Figure 6: SEM image of ONPS0.5 nanoparticles

### 3.4. Surface Wettability and Contact Angle Measurements

Surface wettability of the coatings was evaluated through static water contact angle measurements. The neat epoxy coating exhibited moderate wettability, while coatings containing epoxy-functional silica nanoparticles showed an increased contact angle. This change indicates a modification of surface characteristics resulting from the combined effects of nanoparticle incorporation and epoxy ring functionality.

Table 5: Wettability angle of the samples

Sample Name	Glass Slide	Epoxy (g)	Amorphous Nanoparticles (g)	ONPS Nanoparticles (g)	CNPS Nanoparticles (g)	Contact Angle (°)
CA1	~	–	–	–	–	46.8
CA2	~	1.5	–	–	–	57.19
CA3	~	1.5	0.35	–	–	61
CA4	~	1.5	–	0.35	–	64
CA5	~	1.5	–	–	0.35	72
CA6	~	1.5	–	0.25	0.10	61.5
CA7	~	1.5	–	0.5	–	70
CA8	~	1.5	–	–	0.5	70.5

The presence of epoxy rings at the surface and interface contributes to controlled surface chemistry and micro-scale roughness, which together influence the wetting behavior. The results suggest that epoxy ring functionality can be effectively utilized to tailor surface properties of epoxy-based coatings without compromising structural integrity.



**Figure 9** – Images captured by the contact angle measurement device for samples coated on glass slides are shown. As observed from the images, the contact angle increases with the epoxy coating, and further increases as the nanoparticle content in the epoxy matrix rises. a) bare glass slide, b) glass slide coated with epoxy, c) glass slide coated with a composite of epoxy matrix and amorphous nanoparticles, d) glass slide coated with a composite of epoxy matrix containing 30% GPTMS closed-ring functionalized nanoparticles, e) glass slide coated with a composite of epoxy matrix containing 30% GPTMS opened-ring functionalized nanoparticles.



## **Conclusion**

In conclusion, this study presents a comprehensive and innovative approach to enhancing the hydrophobicity of silica nanoparticles through GPTMS surface modification, with particular emphasis on the mechanistic role of epoxy ring opening. FTIR analysis confirmed successful grafting of GPTMS onto the silica surface, as evidenced by characteristic silane and epoxy peaks, along with subtle shifts indicative of partial epoxy ring opening. This chemical modification provides not only covalent anchoring but also introduces active sites that govern interfacial interactions with water molecules.

SEM imaging revealed a uniform and continuous coating layer on the nanoparticles, preserving nanoscale morphology and preventing significant agglomeration. This structural observation demonstrates that the modification strategy is capable of creating well-defined, stable surface architectures suitable for functional applications. Weight loss analysis indicated enhanced thermal and chemical stability of the modified nanoparticles, highlighting the protective effect of surface grafting and the potential for long-term durability in practical environments.

Zeta potential measurements provided crucial mechanistic insight into the hydrophobic behavior. The opened epoxy rings impart a pronounced negative surface charge, which electrostatically repels polar water molecules, synergistically enhancing the water-repellent effect. This correlation between ring opening, negative zeta potential, and increased contact angle constitutes a key innovation of this study, providing a tunable design parameter for controlling wetting properties.

Integrating chemical, morphological, thermal, and electrostatic analyses, this work establishes a direct link between molecular-level modifications and macroscopic hydrophobic performance. The findings demonstrate that water repellency is not solely dictated by the chemical presence of GPTMS but is critically controlled by the physicochemical effects of epoxy ring opening. This concept—exploiting ring opening to modulate surface charge and hydrophobicity—introduces a new paradigm in surface engineering of nanoparticles. The approach provides a versatile platform for designing advanced water-repellent and anti-wetting nanomaterials with potential applications in protective coatings, self-cleaning surfaces, corrosion-resistant systems, and other functional interfaces.



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