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Silicone Modified Epoxy Resins with Enhanced Chemical Resistance, Corrosion Protection and Hydrophobic Properties

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OUTLINE

- INTRODUCTION
- MOTIVATION
- LITERATURE REVIEW
- EXPERIMENTAL DETAIL
- RESULTS
- DISCUSSIONS
- FUTURE STUDIES

INTRODUCTION

SILICONE RESINS

1. **Fundamental Structure:**
   - Composed of siloxane bonds (Si-O-Si).
2. **Polymeric Network:**
   - Contains organic groups and silicon-oxygen chains.
   - Forms a cross-linked polymeric structure.
3. **Modification with Organic Side Groups:**
   - Typically modified with methyl, phenyl, vinyl, epoxy, or amino functional groups.

Figure 1. General chemical structure of silicone resins. *(Silicones for Coatings, 2023, p. 10)*

Figure 2. Chemical structure of different types of silicone resins *(Silicones for Coatings, 2023, p. 10)*

INTRODUCTION

EPOXY RESIN

1. **Low Molecular Weight Polymers:**
   - Low molecular weight polymers with reactive functionality.
2. **Reactive Resin Structure:**
   - Resins with two or more epoxide groups
3. **Applications in Industry:**
   - Widely used in coatings, adhesives, composites, and electronic encapsulation.

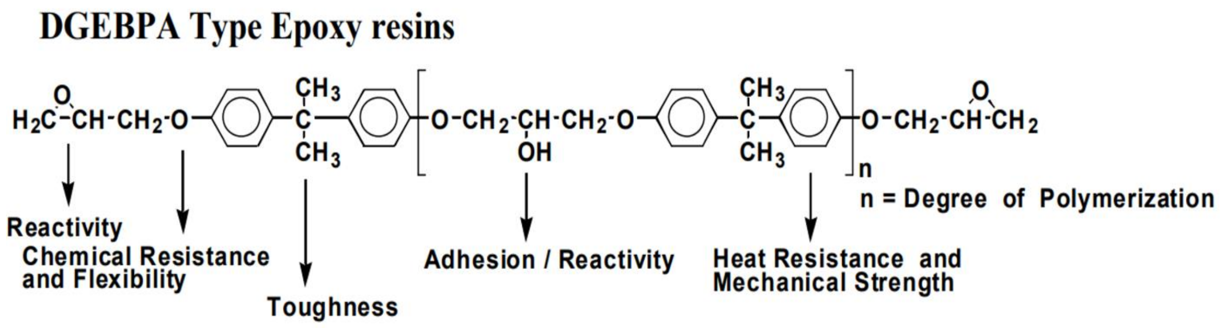

Figure 3. Chemical properties of DGEBPA Type Epoxy *(Kukdo Epoxy Resins & Hardeners, 2003, p. 4)*

INTRODUCTION

DGEBA (Bisphenol-A Type Epoxy)

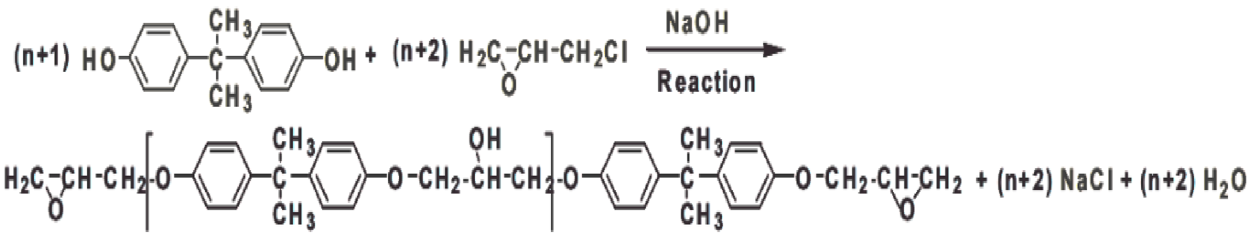

Figure 4. Synthesis mechanism of DGEBA Type Epoxy *(Kukdo Epoxy Resins & Hardeners, 2003, p. 4)*

Hydrogenated DGEBA (Hydrogenated Bisphenol-A Type Epoxy)

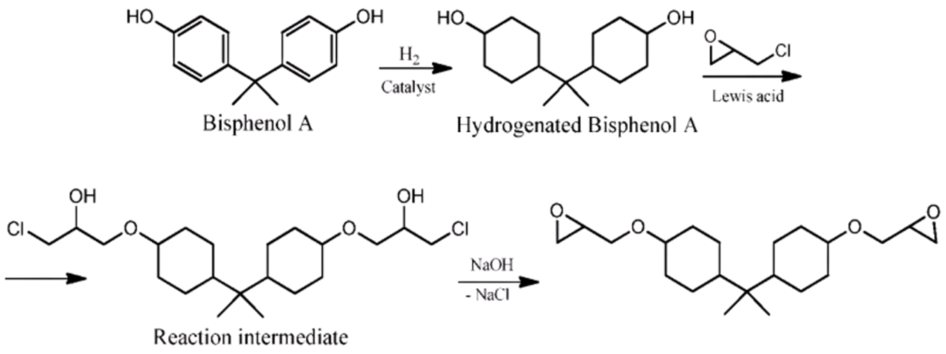

Figure 5. Synthesis mechanism of Hydrogenated DGEBA Type Epoxy *(Tulchinsky et al., Epoxy resin compositions, WO 2015/138128.)*

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MOTIVATION

- ✓ **Investigation of silicone modification of two different epoxy resins:**
  - ❑ DGEBA Bisphenol-A type, (aromatic structure)
  - ❑ Hydrogenated Diphenylpropane (aliphatic structure)

- ✓ **Optimization of key parameters:**
  - ❑ Catalyst type and amount

- ✓ **Investigation the performance of resins synthesized with varying silicone/epoxy ratios.**

- ✓ **Evaluation of the potential use of these modified resins in future anti-graffiti coating systems**

LITERATURE REVIEW

Li et al. (2015) performed a study on the modification of epoxy resins using organosilicon intermediates containing hydroxyl or amine groups.

- **Synthesis strategy**:
  - ✓ Synthesized via **polycondensation**.
- **Reaction conditions**:
  - ✓ Solvent medium: toluene or ethanol
  - ✓ Temperature: ~80–120°C
  - ✓ Silicone content: 5–20 wt%

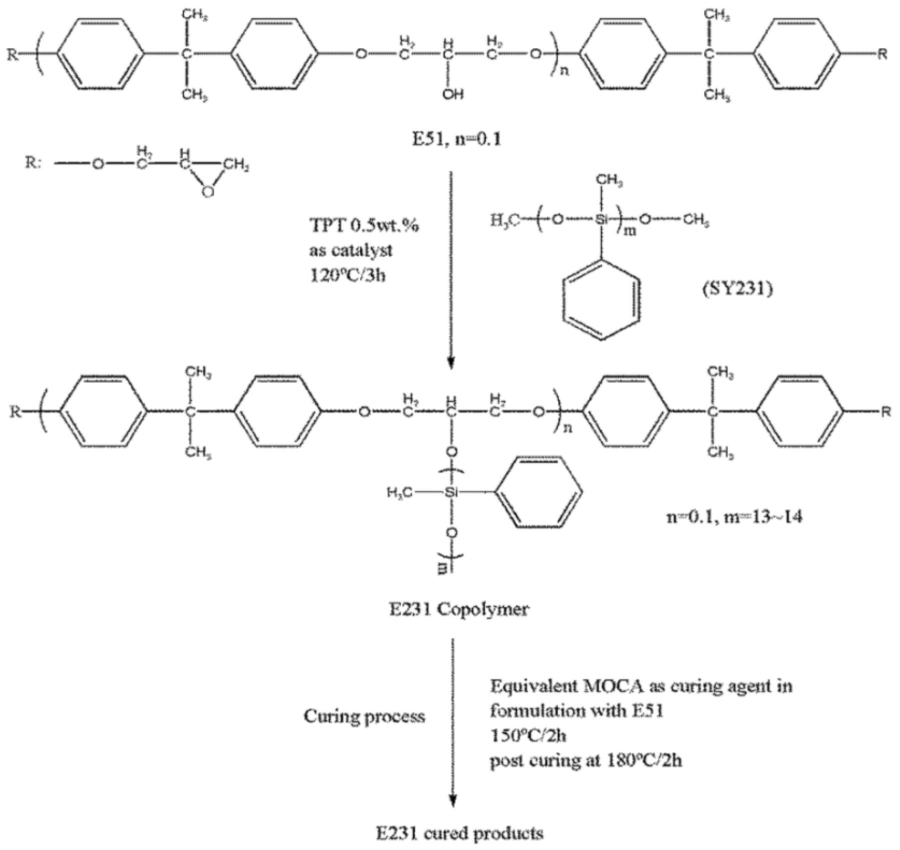

Figure 6. Phase-separated microstructure of polysiloxane-modified epoxy resin *(Li et al., 2015)*

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Li, H.-T., Chuang, H.-R., Wang, M.-W., & Lin, M.-S. (2015). Synthesis, properties and pyrolysis of siloxane- and imide-modified epoxy resin cured with siloxane-containing dianhydride. *Journal of Polymer Research*, 22(1), 1–9.

LITERATURE REVIEW

Yang et al.(2022)study on synthesis of epoxy resin modified with polymethylphenyl siloxane

- **Synthesis strategy**:
  - ✓ Modified using polymethylphenyl silicones, catalyzed by 0.5% DBTD
  - ✓ Alkoxy groups of silicone react with hydroxy groups of epoxy → Si–O–C bonds
  - ✓ Best performance at: 12 wt% polymethylphenyl siloxane , 120°C, 3 hours
- **Reaction conditions**:
  - ✓ In nitrogen atmosphere
  - ✓ Temperature: ~100–130°C, 2-5 h

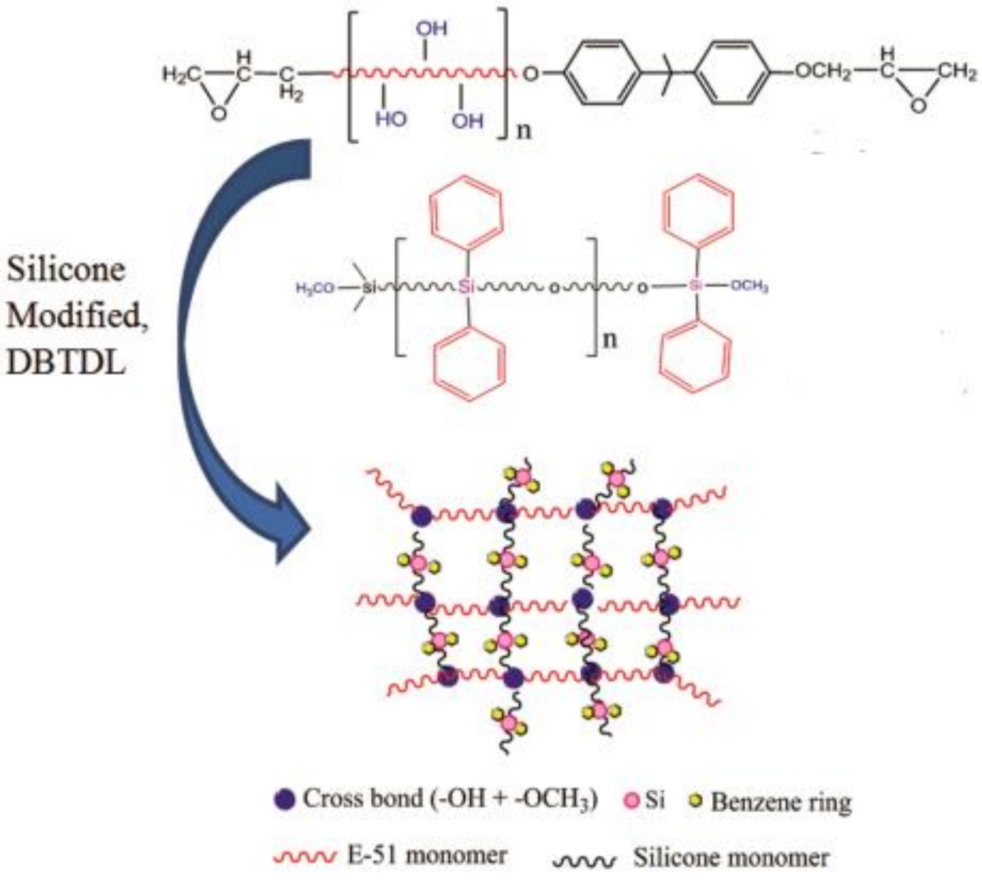

Figure 7. Scheme for silicone modified epoxy resin *(Yang et al 2022.)*

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Yang, Z., Fu, G., & Li, H. (2022). *Synthesis of DC–3074 and Z–1 Silicones Modified Epoxy Resin and Comparison of Salt Spray Resistance*. School of Chemical Engineering, Zhengzhou University; Henan Provincial Engineering Laboratory of Coal-based Ecological Fine Chemicals.

EXPERIMENTAL DETAIL

SYNTHESIS MECHANISM

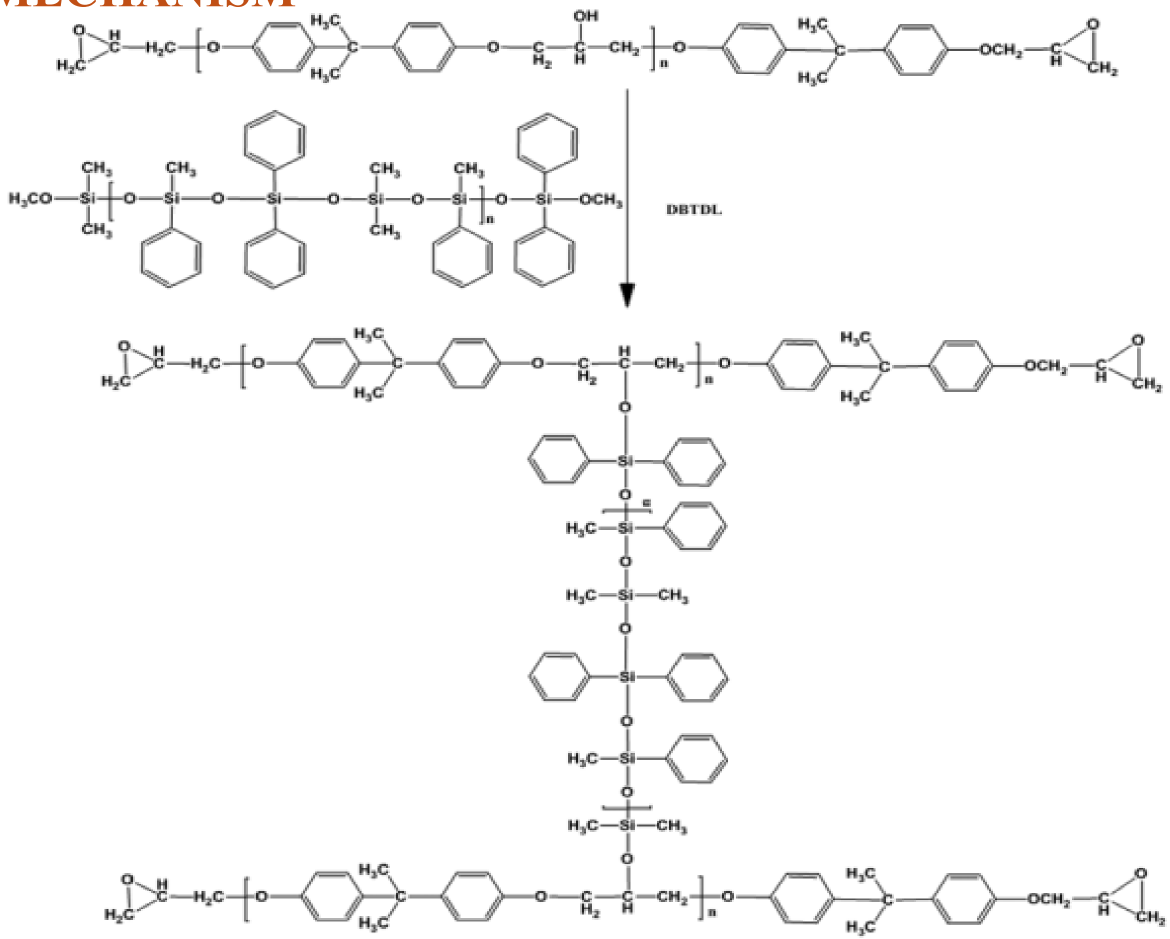

Figure 8. The reaction mechanism of silicone modified epoxy resin *(Yang et al 2022)*

EXPERIMENTAL DETAIL

Table 1. Experimental results of the reactions carried out using tetrabutyl titanate as catalyst.

EX. NAME	EPOXY TYPE	SILICONE TYPE	CATALYST TYPE	EPOXY-SILICONE RATIO	%CATALYST	RESULT
ES-1	Bisphenol-A Type Epoxy	Polymethylphenyl Siloxane	**Tetrabutyl titanate (TnBT)**	3:1	**0,50 %**	• No significant increase in viscosity. •Methanol evolution observed. • Phase separation occurred.
ES-2				3:2		• No significant increase in viscosity. • No methanol detected as a by-product. • Phase separation occurred.
ES-3				1:1		• No significant increase in viscosity. • No methanol detected as a by-product. • Phase separation occurred.

EXPERIMENTAL DETAIL

Table 2. Experimental results of the reactions carried out using tetrabutyl titanate as catalyst with varying catalyst concentrations.

EX. NAME	EPOXY TYPE	SILICONE TYPE	CATALYST TYPE	EPOXY-SILICONE RATIO	%CATALYST	RESULT
ES-4	Bisphenol-A Type Epoxy	Polymethylphenyl Siloxane	**Tetrabutyl titanate (TnBT)**	3:1	**1 %**	• No significant increase in viscosity observed. •Methanol evolution observed. • Phase separation occurred.
ES-5				3:2		• No significant increase in viscosity observed. •Methanol evolution observed. • Phase separation occurred.
ES-6				1:1		• No significant increase in viscosity observed. •Methanol evolution observed. • Phase separation occurred.

EXPERIMENTAL DETAIL

Table 3. Experimental results of the reactions carried out using dibutytin dilaurate as catalyst.

EX. NAME	EPOXY TYPE	SILICONE TYPE	CATALYST TYPE	EPOXY-SILICONE RATIO	%CATALYST	RESULT
ES-7				3:1		• Viscosity increase was observed •Methanol evolution observed. • No phase separation occurred.
ES-8	Bisphenol-A Type Epoxy	Polymethylphenyl Siloxane	**Dibutyltin dilaurate (DBTDL)**	3:2	**0,5 %**	• Viscosity increase was observed •Methanol evolution observed. • No phase separation occurred.
ES-9				1:1		• Viscosity increase was observed •Methanol evolution observed. • No phase separation occurred.

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EXPERIMENTAL DETAIL

Table 4. Experimental results of the catalyst concentrations applied in the synthesis studies involving Hydrogenated Bisphenol-A type epoxy resin

EX. NAME	EPOXY TYPE	SILICONE TYPE	CATALYST TYPE	EPOXY-SILICONE RATIO	%CATALYST	RESULT
ES-10	**Hydrogenated Bisphenol-A Type Epoxy**	Polymethylphenyl Siloxane	Dibutyltin dilaurate (DBTDL)	1:1	**0,50%**	• Viscosity increase was observed. • No methanol was detected as a by-product. • No phase separation occurred.
ES-11				3:1	**1%**	• Viscosity increase was observed. • Methanol evolution was observed. • No phase separation occurred.
ES-12				3:2	**1%**	• Viscosity increase was observed. • Methanol evolution was observed. • No phase separation occurred.
ES-13				1:1	**1%**	• Viscosity increase was observed. • Methanol evolution was observed. • No phase separation occurred.

EXPERIMENTAL DETAIL

Table 5. Selected different epoxy types as experimental parameter

BISPHENOL - A TYPE EPOXY		**HYDROGENATED BISPHENOL A TYPE EPOXY**	
EX. NAME	**EPOXY:SILICONE RATIO**	**EX. NAME**	**EPOXY:SILICONE RATIO**
ES-7	3:1	*ES-11*	3:1
ES-8	3:2	*ES-12*	3:2
ES-9	1:1	*ES-13*	1:1

RESULTS

FT-IR RESULTS

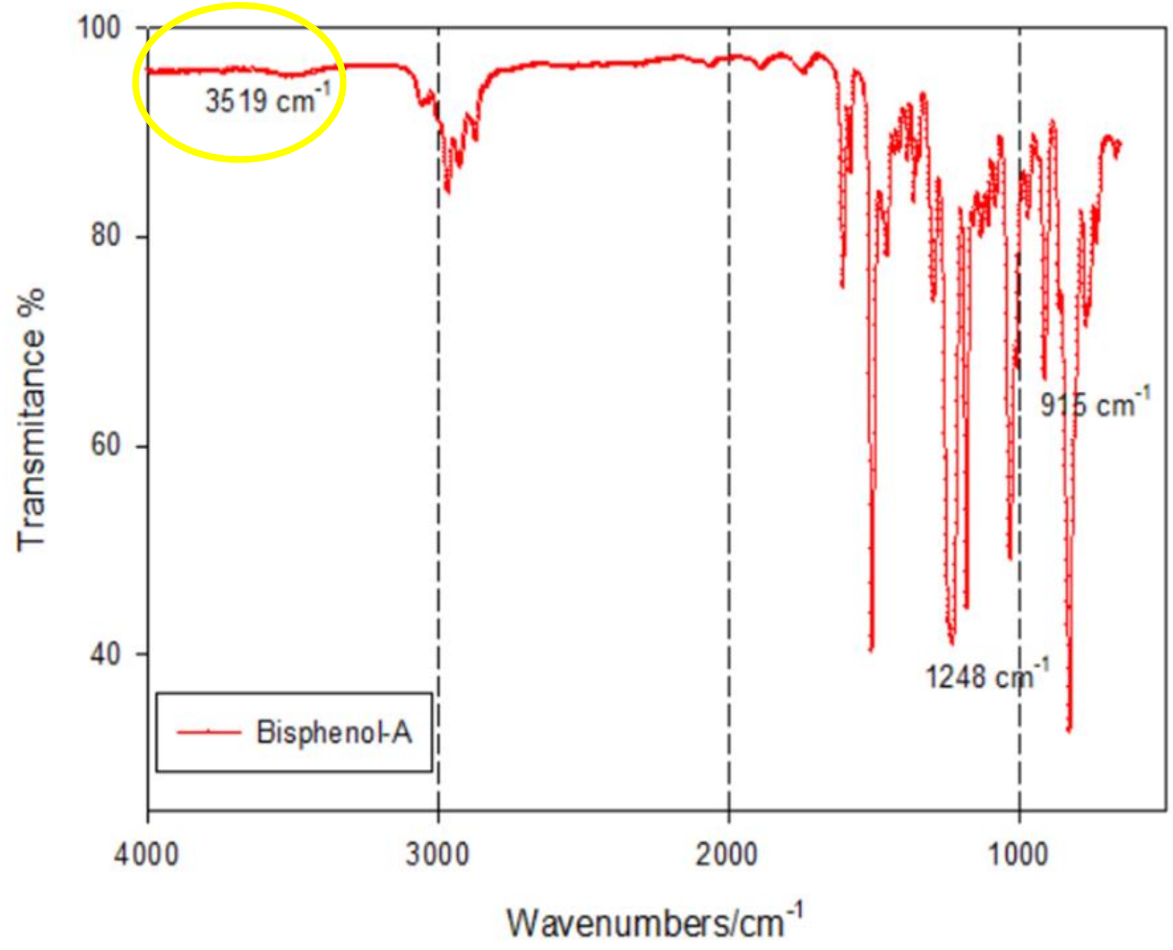
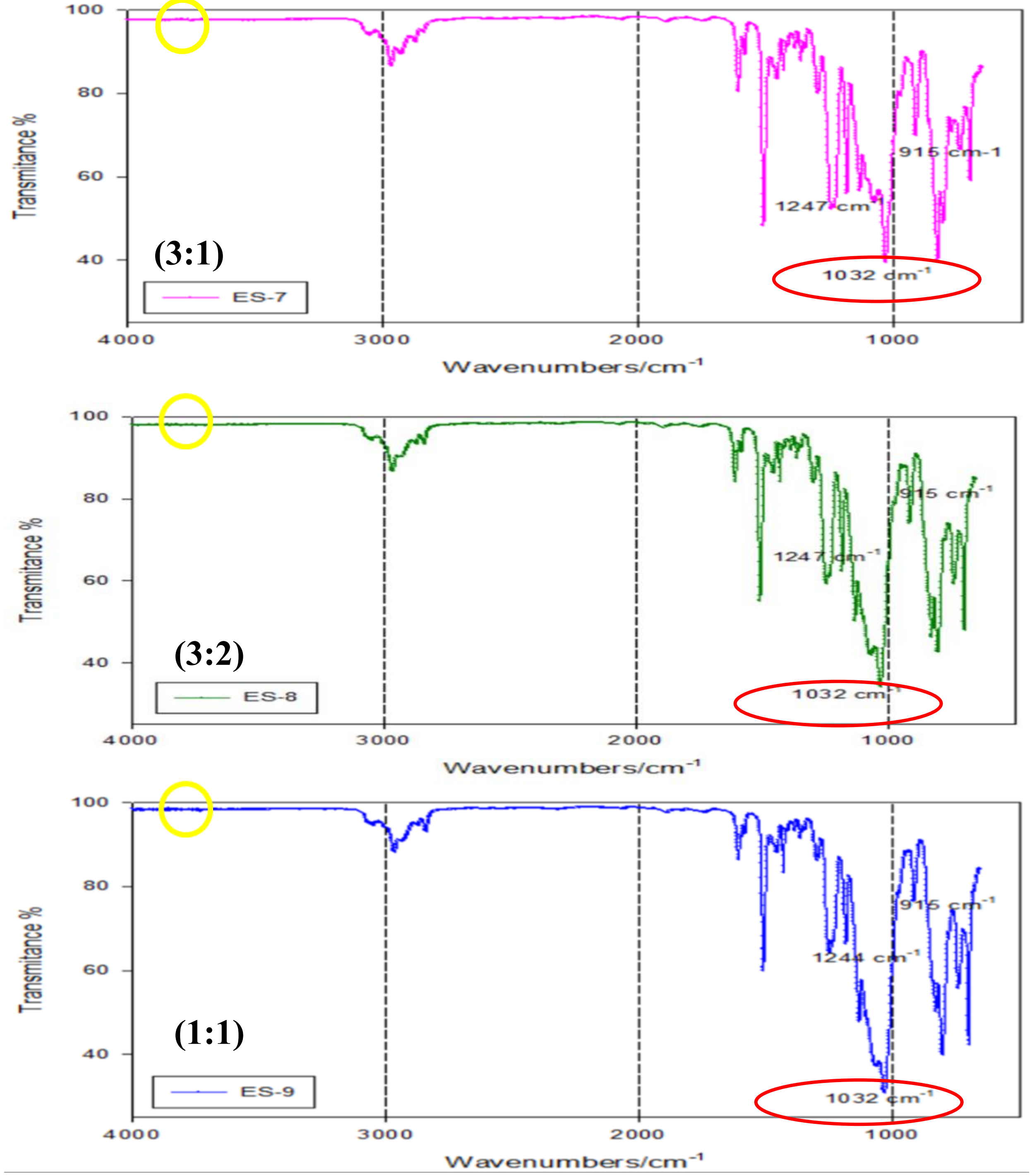


Figure 9. FTIR of bisphenol A type epoxy resin



RESULTS

FT-IR RESULTS

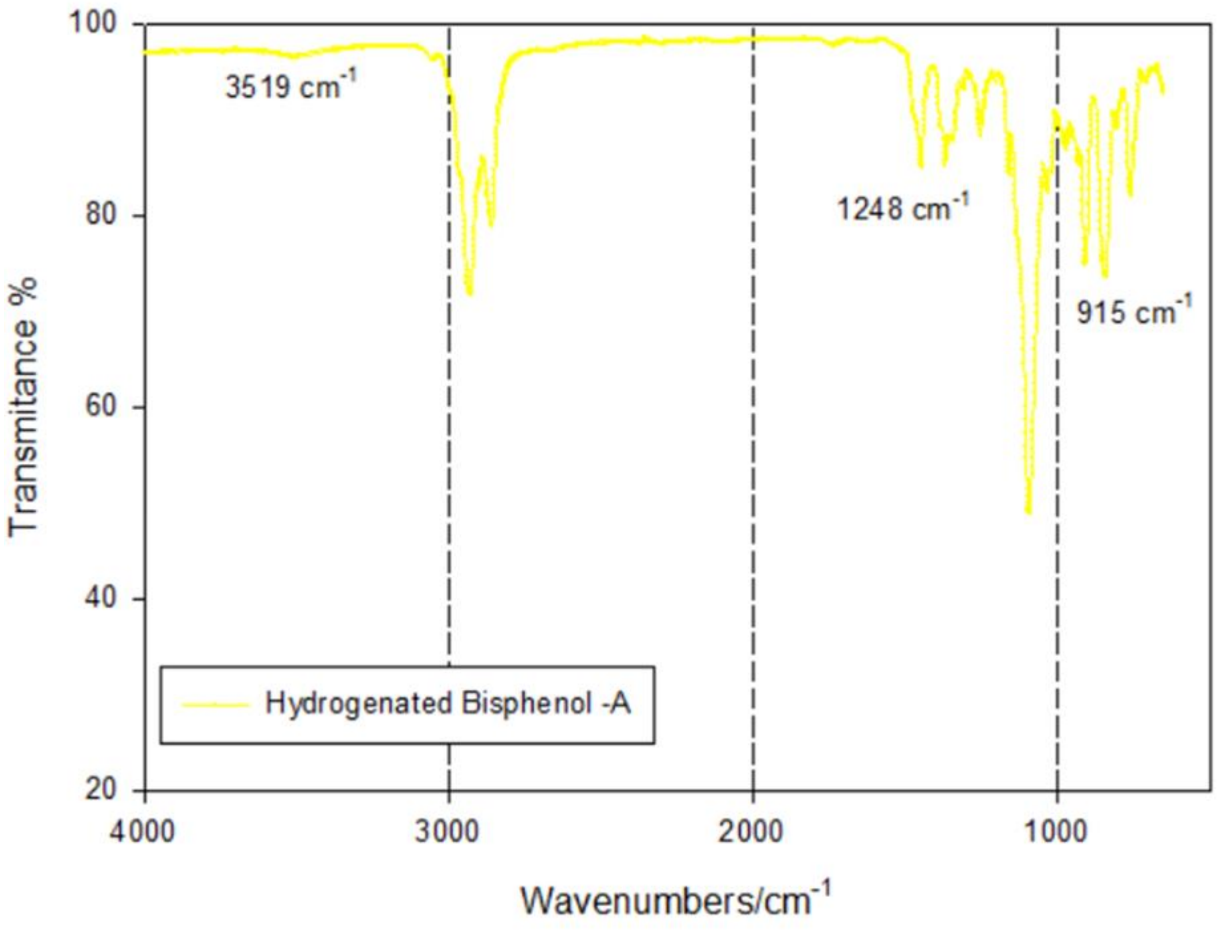
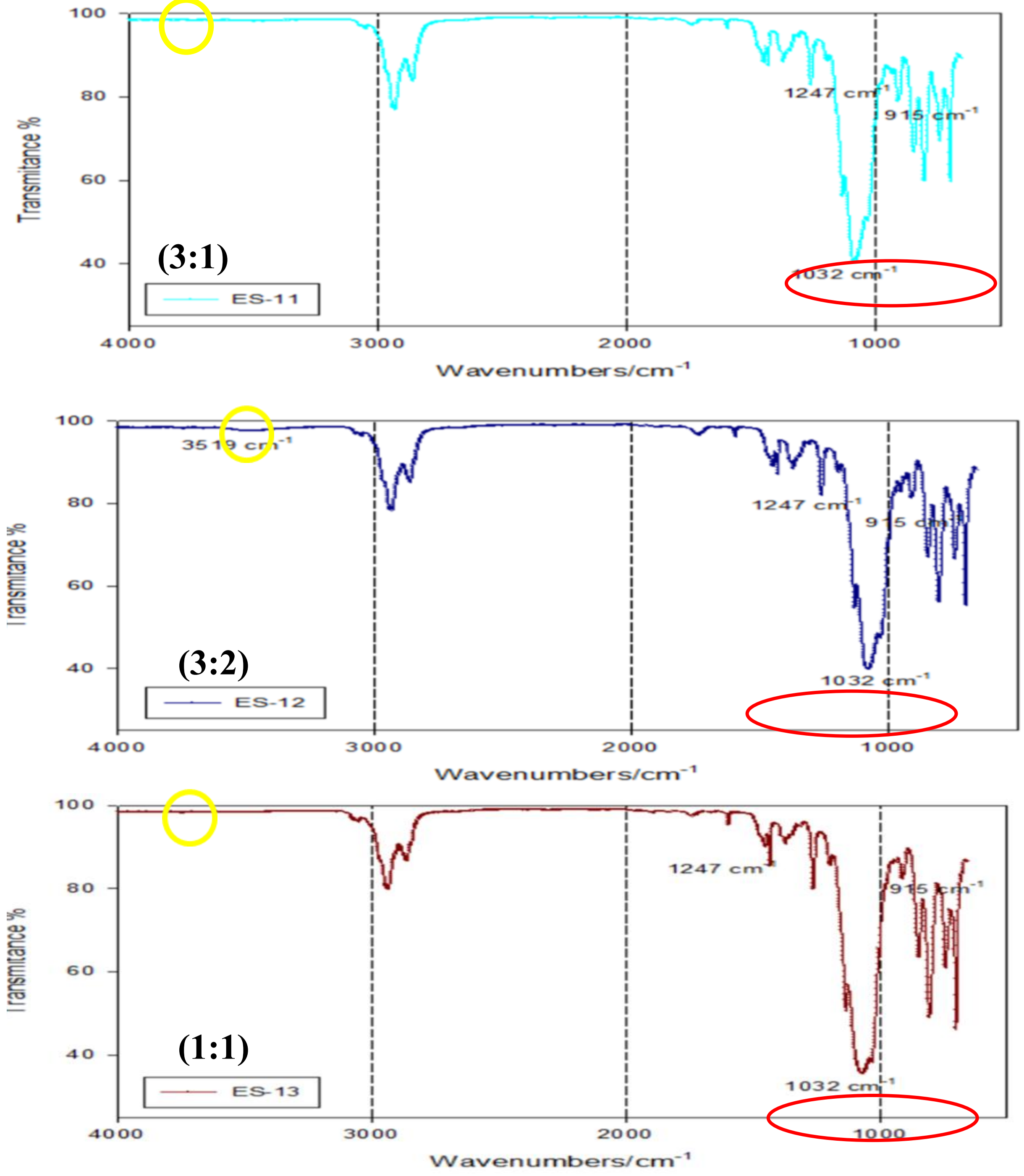


Figure 10. FTIR of hydrogenated bisphenol A type epoxy resin

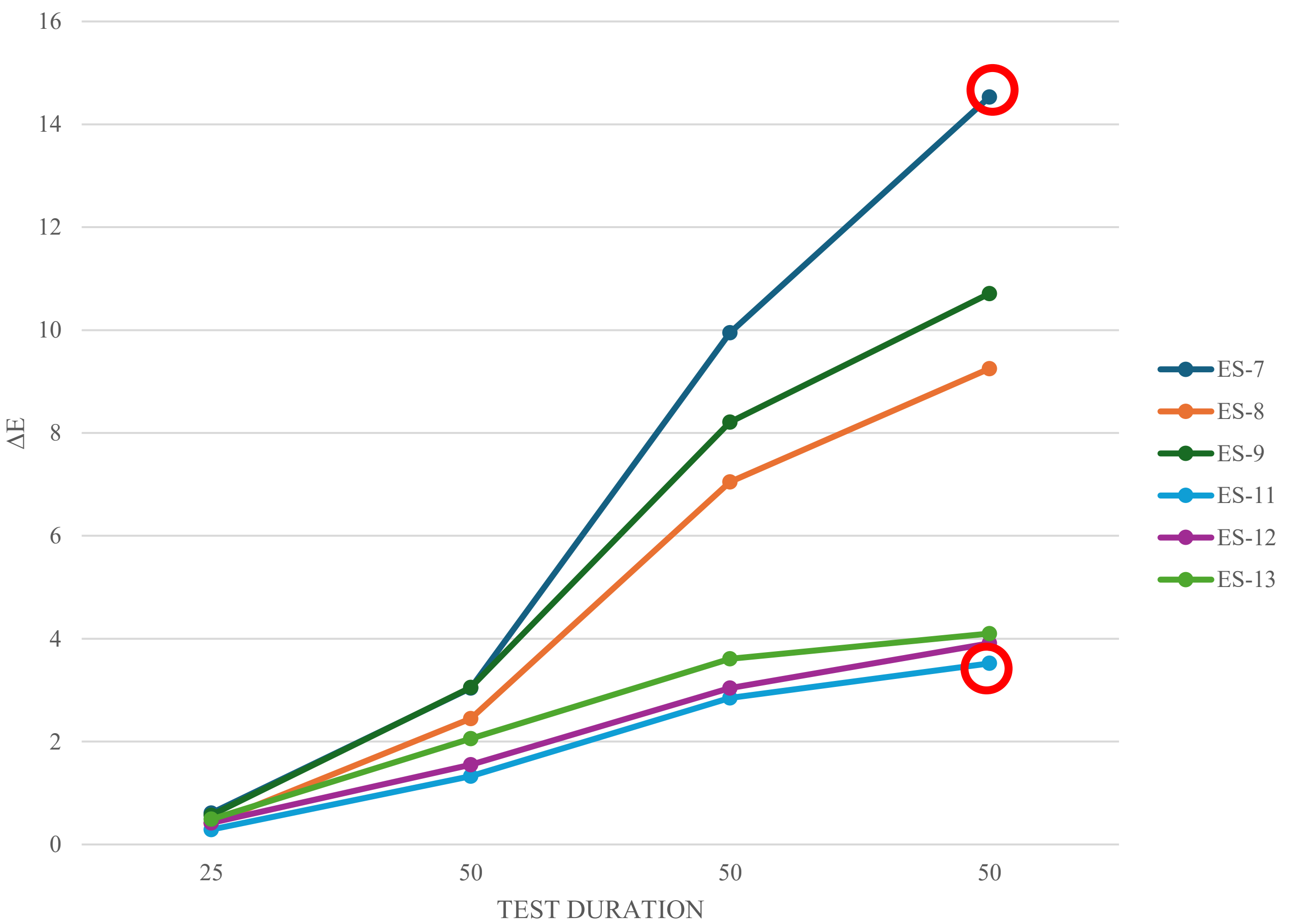


RESULTS

UV RESISTANCE TEST RESULTS

ASTM D 4587-01
UVA-340 Lamp
100 hours

Figure 11. Appearances after 100 hours of UV testing



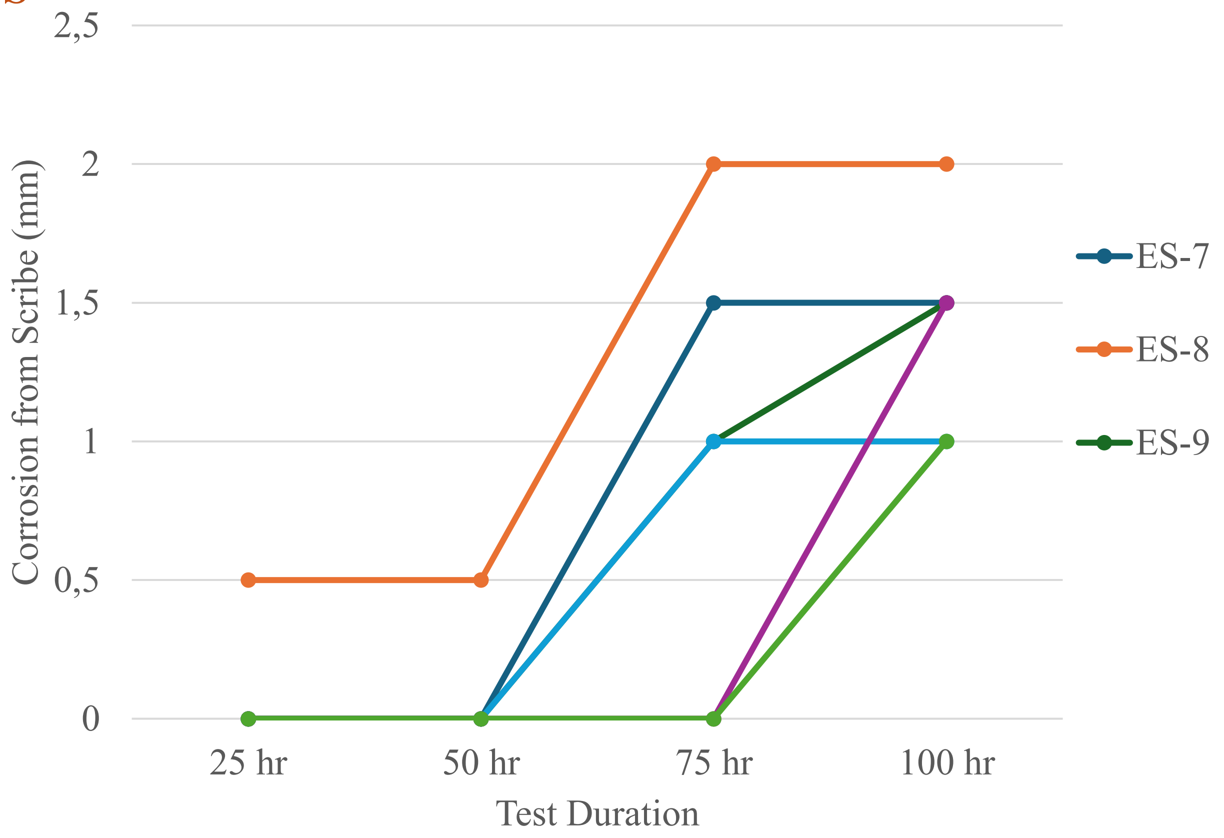
Graph 1. Color stability (ΔE) versus test duration (hr)

RESULTS

CORROSION RESISTANCE TEST RESULTS

ASTM B 117
100 hours

Figure 12. Appearances after 100 hours of corrosion testing

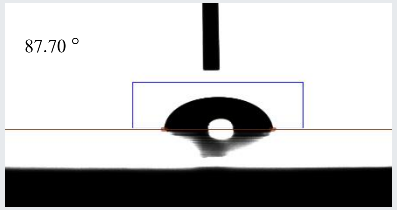
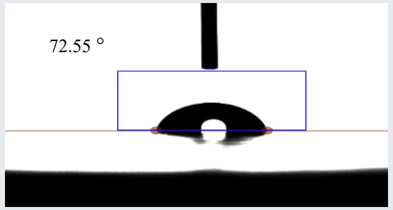
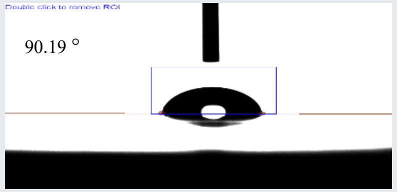
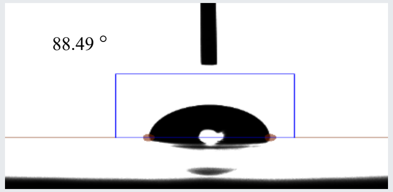
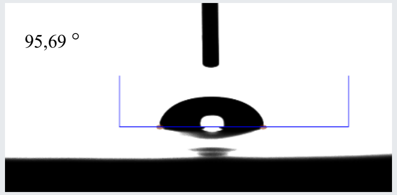
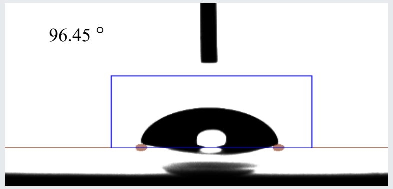


Graph 2. Graph of corrosion from scribe (mm) versus test duration (hr)

RESULTS

CONTACT ANGLE TEST RESULTS

Table 6. Contact angle results

BISPHENOL-A TYPE EPOXY		HYDROGENATED BISPHENOL A TYPE EPOXY	
EX. NAME	**CONTACT ANGLE RESULTS**	**EX NAME**	**CONTACT ANGLE RESULTS**
ES-7		*ES-11*	
ES-8		*ES-12*	
ES-9		*ES-13*	

RESULTS

MEK-RUB TEST RESULTS

ASTM D5402-19

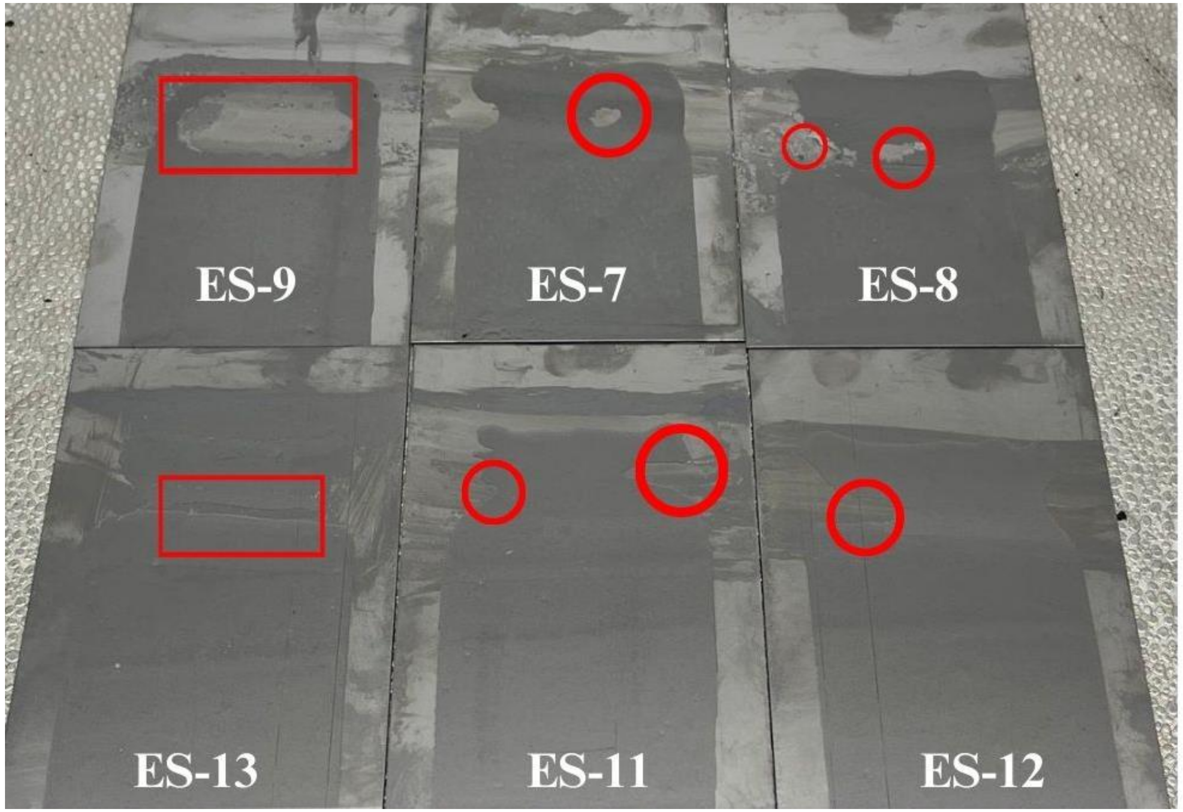


Figure 13. Appearances after MEK double rub test

Table 7. MEK rub test results

EX. NAME	NUMBER OF DOUBLE RUBS
ES-7	63
ES-8	72
ES-9	53
ES-11	89
ES-12	80
ES-13	87

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RESULTS

BRAKE FLUID TEST RESULTS

ISO 2812-3
Brake Fluid - DOT 4
10 min.

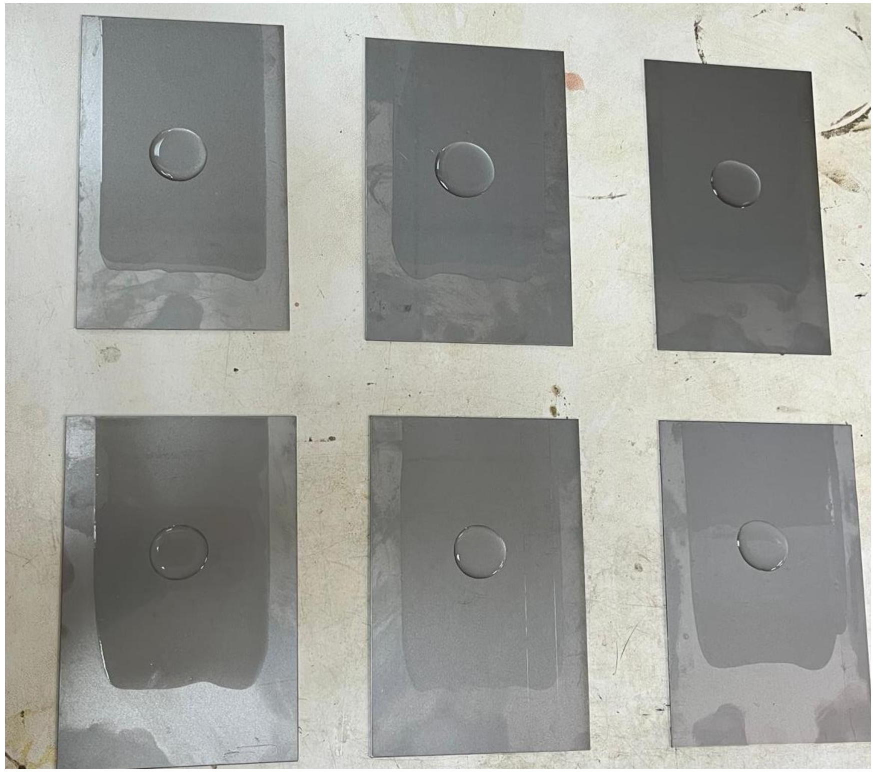

Figure 14. Appearances before break fluid type –DOT 4 test

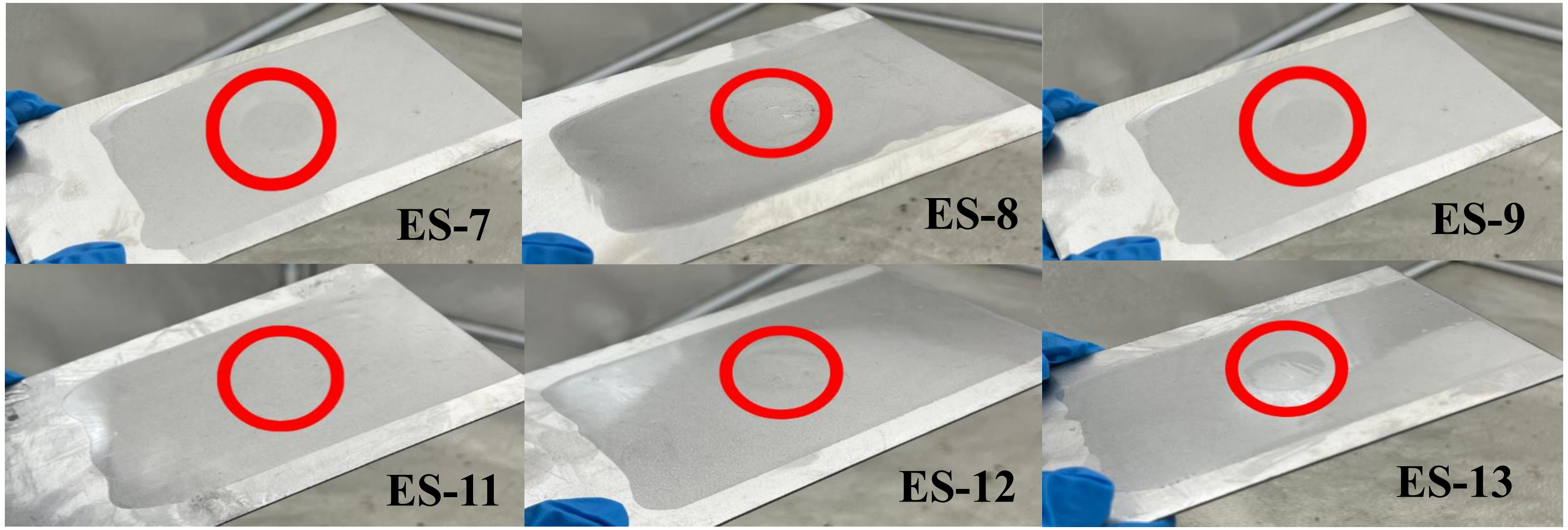

Figure 15. Appearances after break fluid type –DOT 4 test

RESULTS

THE MOST EFFECTIVE RESULTS

Table 10. The most effective results

	ES-7	ES-8	ES-9	ES-11	ES-12	ES-13
UV RESISTANCE				✓		
CORROSION RESISTANCE				✓		✓
CONTACT ANGLE						✓
CHEMICAL RESISTANCE - MEK RUB				✓		
CHEMICAL RESISTANCE - BRAKE FLUID				✓		

DISCUSSION

CATALYST TYPE AND RATIO

- DBTL catalyst was compatible with both Bisphenol-A and Hydrogenated Bisphenol-A Type Epoxy.

FTIR ANALYSIS

- Reduced –OH peaks, indicating successful reaction with silicon alkoxy groups
- Peaks at 1248 cm^{-1} and 915 cm^{-1} confirmed preserved epoxy functionalities.
- Si–O–C peaks (1000–1120 cm^{-1}) indicate successful organosilicon synthesis.

PERFORMANCE TESTS

- UV resistance was highest in ES-11 (Hydrogenated Epoxy); lower silicon content improved stability
- ES-11 showed the best corrosion resistance; lower silicon content was more effective.
- MEK rub tests suggest curing optimization; best result seen in ES-11.
- Chemical resistance slightly improved with higher silicon; no deformation in ES-11.

CONTACT ANGLE ANALYSIS

- Higher silicon content (ES-9, ES-13) increased hydrophobicity (contact angle: 100–120°).

FUTURE STUDIES

- The performance of the resin in paint systems will be evaluated.
- Epoxy resins will be modified using various silane compounds.
- Corrosion resistance will be analyzed using Electrochemical Impedance Spectroscopy (EIS).
- The effects of different epoxy-to-silicon ratios will be investigated.
- Different types of silanes will be tested to achieve hydrophobic behavior.
- Resins will be developed for use in anti-graffiti and anti-fouling coatings.

THANK YOU FOR ATTENTION !

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