

Synthesis, Characterization, and Application of Poly(Styrene-Co-Glycidyl Methacrylate) as Reactive Diluents to Epoxy Resin

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Abstract. Anticorrosion coatings are specialized products designed to protect metal surfaces from costly and dangerous corrosion, acting as barriers against corrosive organisms. Therefore, this study examined the physical and mechanical properties of epoxy resin in the presence of reactive diluents. Reactive diluents were synthesized based on styrene (St) and glycidyl methacrylate (GMA) through the free radical method using benzoyl peroxide (BPO) as a catalyst with various feed ratios of St and GMA. Diluents were characterized by Fourier Transform Infrared (FTIR) spectroscopy and Thermogravimetric Analyzer (TGA). Epoxy resins and hardener were at a ratio of 1:1, 1:0.5, and 1:0.3, respectively. The results showed that reactive diluents [Poly(St-co-GMA)] had an excellent dilution effect on epoxy resin with a decrease in epoxy resin viscosity from 8592 mPa-s to 1656, 680, and 430 mPa-s. Furthermore, the adhesion, tensile, and hardness properties contained 70% GMA and 30% St at a hardener ratio of 1:0.3. The increase in the mechanical properties was attributed to the reaction between modified epoxy resins with hardener.

Keywords: Epoxy; Hardener; Mechanical properties; Reactive diluents; Styrene

1. Introduction

Corrosion is a natural process that causes metal surfaces to degrade and fail, posing potential costs and hazards. These surfaces can be protected with anticorrosion coatings, which serve as barriers against corrosive organisms (Ainakulova *et al.*, 2023; Ningrum *et al.*, 2023; Devianto *et al.*, 2023; Riyanto *et al.*, 2023). Various anticorrosion coatings offer unique properties and application methods, among which the organic types are potentially

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helpful in preventing corrosion on metal surfaces (Msekh *et al.*, 2018; Fu and Cheng, 2011). Some recently improved methods include epoxy polymers, characterized by excellent adhesion, chemical resistance, and durability properties. Most epoxy resins comprised aromatic rings and two heteroatoms, namely P, O, N, and S (Dagdag *et al.*, 2020; Makhoulouf, 2014). Hardener or cross-linking agent plays an important role in curing epoxy resins at room temperature. The mechanical properties of these resins depend on the type and characteristics of hardener, such as concentration and temperature (Najuma and Lity, 2014; Jain *et al.*, 2006). Furthermore, reliable analytical methods that efficiently measure the groups in epoxy resins are crucial for synthesis and product quality control. The different application methods require low viscosities, particularly in coating industries. Meanwhile, reducing epoxy resin viscosities often entailed using organic solvents, which can harm both health and the environment (Pineda *et al.*, 2016). The preliminary study focused on the exploration of alternative methods, such as reactive diluents rather than organic solvents. These diluents typically contained oxirane ring compounds, namely glycidyl methacrylate, benzyl glycidyl ether, 1, 4-butanediol diglycidyl ether, etc (Jingyu, Haichao, and Guoxin, 2022; Tran *et al.*, 2020). Polymers with epoxide groups, such as glycidyl methacrylate (GMA), are categorized as epoxy resins (Tzoumani *et al.*, 2022) and have been widely used in a variety of applications, including surface coatings, electrical laminates, adhesives, and molding compounds (Pramanik, Mendon, and Rawlins, 2012; Teh *et al.*, 2007; Wang *et al.*, 2005). Epoxy groups in polymers significantly impact the effective performance in diverse applications (Maruyama, 2001), which enable GMA-based copolymers to enhance coating adhesion, barrier properties, corrosion protection, and service life. Meanwhile, free radical solution polymerization offered advantages such as block copolymers with monomers (Asha *et al.*, 2019). Azzahari *et al.* (2012) used free radical polymerization in toluene with BPO as an initiator to produce new copolymers from various feed compositions of GMA and tetrahydrofurfuryl acrylate (THFA). The thermal stability of copolymers rises as the THFA content increases. Srikanth *et al.* (2007) carried out a research to determine the methods needed to produce copolymers from different feed ratios of N-(acryloyloxymethyl) benzotriazole (AMBT) and GMA using the free radical solution polymerization process. Epoxy groups in acrylate anticorrosion coatings produced densely packed, cross-linked coatings, which enhanced corrosion protection due to the stronger chemical bonds. The result improved corrosion protection and prolonged service life for the coated metal substrates. Therefore, this study aimed to prepare Poly(St-co-GMA) copolymers as reactive diluents to reduce viscosity of epoxy resin as well as improve the physical and mechanical properties, including adhesion and thermal characteristics in the presence of an amine-based hardener at a ratio of 1:1, 1:0.5 and 1:0.3. During copolymerization process with GMA, styrene (St) played a critical role by increasing the rate of polymerization and improving the mechanical properties of epoxy resins such as thermal, mechanical, and chemical resistance (Mehmet, 2000). The prepared Poly(St-co-GMA) copolymers were characterized using Fourier Transform Infrared (FTIR) spectroscopy and Thermogravimetric Analyzer (TGA).

2. Methods

2.1. Materials

Epoxy resins ELM-NG 1000 and hardener ELM-NG 34H were supplied by Elcos Marketing LLP, Kazakhstan. ELM-NG 1000 had an epoxy value ranging from 5.25 to 5.5 eq/Kg, with a weight per epoxide, viscosity, and density of 182 g/eq, 8500 mPa-s at 25°C and 1.16 gm/cm³, respectively. Meanwhile, ELM-NG 34H had an amine value and viscosity of 298 mgKOH/g and 254 mPa-s at 25°C. Major chemicals, namely glycidyl methacrylate

(GMA \geq 97%), St, xylene, and benzoyl peroxide (BPO) were purchased from Sigma-Aldrich and used as received.

2.2. Synthesis of Poly(St-co-GMA) copolymer

Copolymerization process included combining St and GMA with different feed monomer compositions, namely M1= 70/30, M2= 50/50, and M3 = 30/70, using the free radical polymerization method in the presence of xylene as a solvent. The solution medium was put into a 500 mL three-necked flask system equipped with a stirrer, reflux condenser, and thermometer. The catalyst BPO was added to the flask while stirring mechanically at 500 to 600 rpm, maintaining a temperature of 65°C using an automatically controlled water bath under the atmosphere. After achieving complete solubility, the required amount of St and GMA monomers were added dropwise during stirring, and the reaction proceeded for 2 hours at 80°C, followed by another 1 hour at 90°C.

2.3. Characterization of Poly[St-co-GMA] copolymer

The prepared Poly[St-co-GMA] copolymer was characterized using ALPHA FTIR spectroscopy, Bruker. FTIR spectroscopy and TGA were used to identify and study the functional groups of copolymers and the thermal properties, respectively. The per-dried copolymers were tested using Perkin Elmer TGA (TGA/SDTA851e, METTLER TOLEDO, Switzerland). Furthermore, the measurements were carried out at room temperature and heating rates of 900°C and 10°C/min under the atmosphere.

2.4. Tests

The viscosity (mPa-s) of epoxy resins and reactive diluents were measured at room temperature using a Brookfield viscometer, according to ISO 12058-1 (ISO, 2018), at a speed of 5 and 50 rpm. Meanwhile, epoxy value (eq/Kg) and weight per epoxide g/eq of resins were determined using the titration method at room temperatures according to ASTM D1652. The properties of reactive diluents and modified epoxy resins are shown in Tables 1 and 2, respectively.

Table 1 Properties of reactive diluents.

| Reactive diluents | M1 | M2 | M3 | Test method |
|--------------------------|-----------|-----------|-----------|-------------|
| Viscosity, mPa-s | 10 | 14 | 35 | ISO 12058-1 |
| Epoxy value, eq/Kg | 0.31-0.33 | 0.35-0.37 | 0.40-0.43 | ASTM D1652 |
| Weight per epoxide, g/eq | 130.5 | 138.6 | 142.5 | ASTM D1652 |

2.5. Mixing ratio

Epoxy resins (E0, 90 %) were mixed with reactive diluents (10%) labeled M1, M2, and M3 using a stirring stick or spatula for 10 minutes, which led to the formation of epoxy resins denoted as EM1, EM2, and EM3. Additionally, the properties of these epoxy resins are shown in Table 2.

ELM-NG 34H is a low-viscosity modified cycloaliphatic that functions as hardener when mixed with epoxy resins in different ratios of 1.0:1.0, 0.5:1.0, and 0.3:1.0. To ensure proper blending, mix the ingredients slowly and deliberately, making sure to scrape the container for thorough incorporation. Finally, apply the epoxy mixture to metal and concrete substrates, and allow it to cure naturally at room temperature.

Table 2 Properties of epoxy resin mixed with reactive diluents.

| Modified epoxy with reactive diluents | EM1 | EM2 | EM3 | Test method |
|---------------------------------------|-----------|------------|-----------|-------------|
| Viscosity, mPa-s | 430 | 680 | 1656 | ISO 12058-1 |
| Epoxy value, eq/Kg | 4.4 - 4.9 | 4.10 - 4.8 | 4.1 - 5.2 | ASTM D1652 |
| Weight per epoxide, g/eq | 195 | 210 | 230 | ASTM D1652 |

2.6. Film preparation

Epoxy resin (E0) and mixtures with reactive diluents were mixed in a beaker with different hardener ratios of 1:1, 1:0.5, and 1:0.3 to ensure homogeneity. The resulting mixtures were poured into steel molds, forming specimens with dimensions of 7 mm x 7 mm x 7 mm, and allowed to dry at room temperature for 6 days (Negim *et al.*, 2011). The process of mixing and casting is shown in Figure 1.

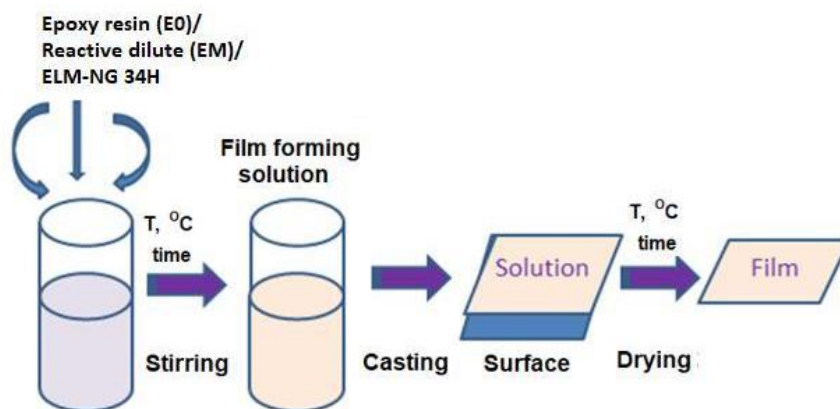


Figure 1 The process of mixing and casting for film preparation.

2.7. Mechanical Tests

Steel films of 12 cm x 6 cm x 1 mm were provided to evaluate mechanical properties and chemical durability during curing. A cylindrical Mandrel Tester (ASTM D522) (ASTM, 2001) was used to assess the resistance of a coated product to cracking and detachment from a metal substrate when subjected to bending under standard conditions. The tubular impact (ASTM D2794) (ASTM, 2019) and the economic cross-hatch testers (ASTM D3359) (ASTM, 2001a) were used to evaluate the film resistance to impact and adhesion of applied coatings, respectively. Additionally, the adhesion strength measurements of epoxy and diluted mixture were conducted using pull-out tests according to EN 1542 standard (Krzywiński and Sadowski, 2019).

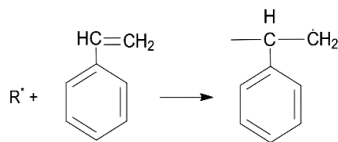
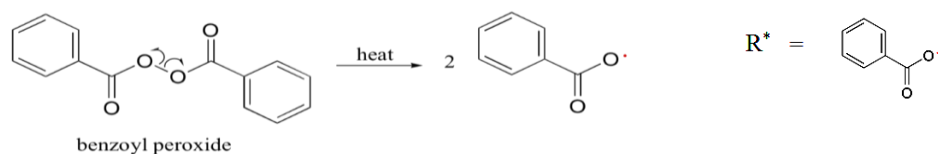
3. Results and Discussion

3.1. Copolymerization

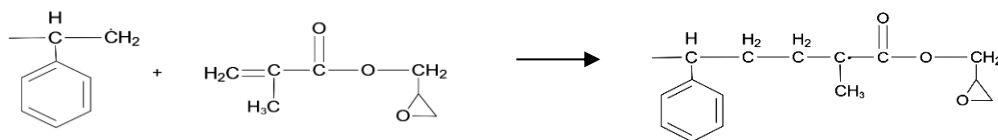
An overview of copolymerization process of Poly(St-co-GMA) is shown in Figure 2. This reaction mechanism comprised three distinct steps, initiation (I), propagation (II), and termination (III), conducted at a temperature of 80°C for 1 hour.

Several factors, such as monomer reactivity, initiator selection, reaction conditions, and kinetics, must be considered to successfully copolymerize St and GMA. The reactivity ratio of the monomers determined the composition and structure of copolymer. The initiator, typically a free radical, must be compatible with the monomers, desired reaction and decomposition temperatures, solubility, and reactivity. Copolymerization process relied on specific reaction conditions, namely temperature, solvent, and time. The temperature, solvent and reaction time must be suitable for reactivity, compatible, and adequate to complete the process. According to Tzoumani *et al.* (2022), reaction kinetics played a crucial role in determining the composition and molecular weight distribution of copolymer (Tzoumani *et al.*, 2022).

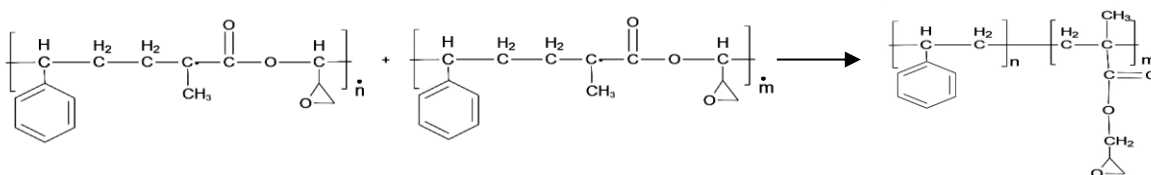
I. Initiation



II. Propagation



III. Termination

**Figure 2** Mechanism of copolymerization Poly(St-co-GMA).

3.2. FTIR spectral analysis of Poly(St-co-GMA)

Figure 3 shows FTIR absorption spectra of GMA, where peaks in 942.18 cm^{-1} to 814.57 cm^{-1} were attributed to the oxirane ring in the structure (Zhao *et al.*, 2018). The intensive peak at 1716.38 cm^{-1} represents the stretching vibration of C=O in carbonyl groups. In addition, the peak at 1154.49 cm^{-1} was attributed to C-O stretching of aliphatic ether (Rajiv *et al.*, 2017). The main difference observed in FTIR spectra of copolymer St-co-GMA was the presence of absorption bands at 2923 cm^{-1} and 2850 cm^{-1} , attributed to CH₂ asymmetric stretch. The two peaks at 1632 cm^{-1} and 1490 cm^{-1} were related to the aromatic ring mode from St (Hermán *et al.*, 2015). Significant differences in the intensity of the spectra are observed in the range from 993.17 cm^{-1} to 845.94 cm^{-1} , representing the oxirane ring. Significant differences in the intensity of the spectrum were observed in the range of 993.17 cm^{-1} and 845.94 cm^{-1} . This absorption region represented the oxirane ring, which is suitable and responsible for the material's epoxy groups and high properties. The differences in intensity corresponded to the ratio of initial components. The more intensive peaks absorbed, the greater the amount of reacted GMA.

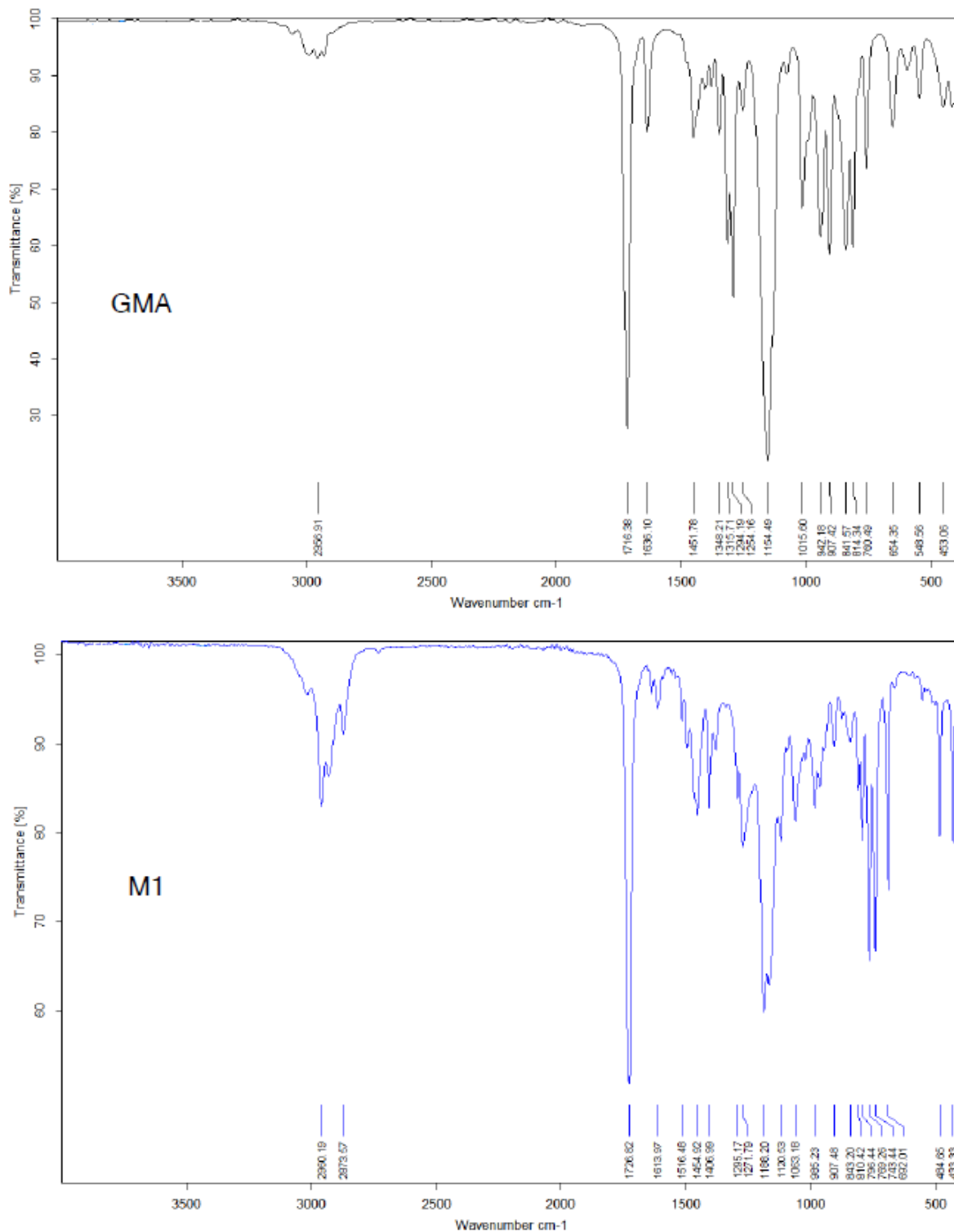


Figure 3 FTIR spectra for poly GMA, M1 and M2. Copolymerization process included combining St and GMA with different feed monomer compositions, namely M1= 70/30, and M2= 50/50

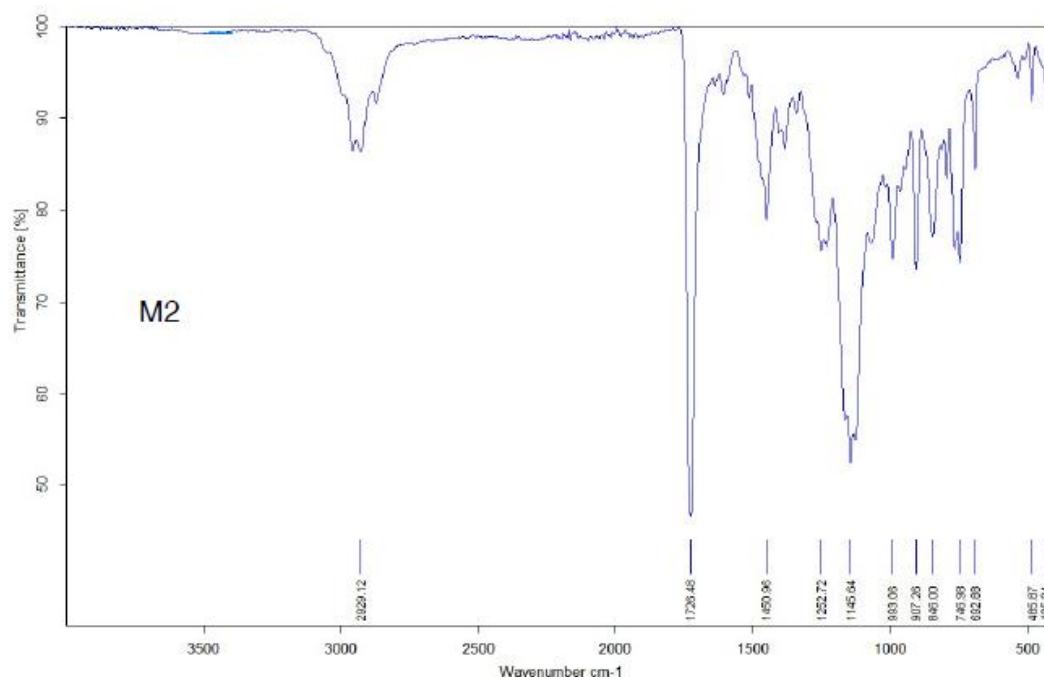


Figure 3 FTIR spectra for poly GMA, M1 and M2. Copolymerization process included combining St and GMA with different feed monomer compositions, namely M1= 70/30, and M2= 50/50 (Cont.)

3.3. Thermal properties of Poly(*St-co-GMA*)

TGA was used to examine the thermal stabilities, including the impact of various St and GMA ratios on weight loss in copolymer. TGA thermograms of Poly(*St-co-GMA*) with various ratios are in Supplementary 1 (S1). Meanwhile, Table 3 shows the initial decomposition and maximum polymer degradation temperatures (PDT_{max}), as well as weight loss (%) after thermal decomposition.

TGA curves showed that copolymers experienced three-step degradation processes for M1, M3 and two steps for M2. The temperature range in the first stage was between 0°C and 170°C, while the weight loss (%) increased with higher GMA content, attributed to bound water or impurities. M3 and M1 showed the highest and lowest weight loss of 29% and 9%, respectively. In the second stage, weight loss for M1 and M3 started at 170°C and continued to 340°C, while for M2, it extended from 210°C to 900°C, corresponding to the ester decomposition and loss of CO₂ (Negim *et al.*, 2014; Vitaliy *et al.*, 2003). The analysis led to a higher weight loss for M2 than M3 and M1. The weight loss for the third stage started at 340°C and continued to 900°C for M1 and M3. However, an increase in the GMA ratio caused a decrease and an increase in the weight loss for M3 (19%) and M1 (29%) due to GMA decomposition. Copolymer, with increased GMA content, showed exceptional thermal stability and versatility, making it suitable for various applications. The maximum polymer degradation (PDT_{max}) was related to the temperature where the highest rate of weight loss occurred, and it increased as GMA content in copolymer decreased. Meanwhile, M1 and M3 showed the highest and lowest PDT_{max} of 400°C, and 180°C, respectively.

High thermal degradation resistance in materials offered several advantages, namely structural integrity and performance stability, which made it suitable for high-temperature applications such as automotive components, electronic devices, and aerospace, ensuring longevity and reliability. According to Ramezani *et al.* (2023), thermal degradation is a process where the mechanical properties of a material, such as strength and toughness, deteriorate.

High thermal degradation resistance enabled a material to maintain the properties even under increased temperatures, improving durability and safety. This extends the shelf life of the material, reducing the need for frequent repairs, thereby leading to cost savings and increased efficiency. High thermal degradation resistance enhanced stability, mechanical properties, extended shelf life, and thermal cycling resistance. The degradation process is important in demanding environments under elevated temperature conditions (El-Gamal *et al.*, 2023).

Table 3 Thermal properties of Poly(St-co-GMA) at different feed ratios

| Sample (%) | Temperature (°C) | Weight loss (%) | PDT _{max} (°C) |
|------------|------------------|-----------------|-------------------------|
| M1 | 0 -170 | 9 | 400 |
| | 170 -340 | 26 | |
| | 340 -900 | 29 | |
| M2 | 0 -210 | 12 | 320 |
| | 210 -900 | 55 | |
| M3 | 0-180 | 21 | 180 |
| | 180 -330 | 40 | |
| | 330 -900 | 16 | |

3.4. Applications with epoxy

3.4.1. Viscosity

Viscosity of epoxy resin (E0) mixed with 10% reactive diluents of varying composition ratios was measured at different speeds (5 and 50 rpm) and 25°C, as shown in Table 4. The results depicted that as the viscosity of E0 decreased, the spindle speed increased, a phenomenon attributed to the orientation of polymers in the flow direction and chain deformation (Devrani *et al.*, 2017). Viscosity of epoxy resin decreased when mixed with reactive diluents, from 8592 mPa-s to 430 mPa-s, 680 mPa-s, and 1656 mPa-s for EM1, EM2, and EM3, respectively. However, viscosity of epoxy resin increased with a higher ratio of GMA in reactive diluents. The increase was attributed to the dilution effect of reactive diluents on epoxy resin and the subsequent increase in weight per epoxide (g/eq) between cross-linking points (Malburet *et al.*, 2023; Rudawska and Frigione, 2022; Jagtap and More, 2021; Negim *et al.*, 2021; Ozeren and Ozkul, 2018). Viscosity and thixotropic index are important factors when applying epoxy resins spatially to metal and concrete substrates. The thixotropic index is a ratio of viscosities at low and high speeds by a factor of ten. The effect of reactive diluents with different compositions on Thixotropic index (TI) of epoxy resin is shown in Table 5. TI of epoxy resin (E0) was 3.58, decreasing to less than 1 when epoxy resin was diluted with reactive diluents. Furthermore, TI of diluted epoxy resin increased with a higher ratio of GMA in reactive diluents.

Table 4 Viscosity and thixotropic index of epoxy resin mixed with reactive diluents.

| Sample code | E0 | EM1 | EM2 | EM3 |
|-----------------------------|------|------|------|------|
| Viscosity at 5 rpm (mPa-s) | 8592 | 430 | 680 | 1656 |
| Viscosity at 50 rpm (mPa-s) | 2400 | 1400 | 1150 | 1700 |
| Thixotropic index (TI) | 3.58 | 0.31 | 0.59 | 0.97 |

3.4.2. Adhesion

The adhesion strength of epoxy resin to concrete and metal substrates is an important parameter in surface bonding (Naderi, 2008). The effect of reactive diluents with different compositions on the adhesion strength of epoxy on these surfaces is shown in Table 5. It was reported that as hardener ratio increased from 0.3 % to 1.0%, the adhesion strength of epoxy resins mixed with reactive diluents decreased. The decrease was attributed to the type and

ratios of hardener (Vidil *et al.*, 2016; Negim *et al.*, 2011). The mixed epoxy resin with reactive diluents increased the adhesion strength compared to the reference epoxy resin (E0). The rise was due to the presence of epoxy ring in GMA and increased cross-linking resulting from the interaction between the rings from epoxy resin and reactive diluents with hardener (Thakor *et al.*, 2021). However, the adhesion strength of epoxy mixture on the concrete and metal substrates increased with the content of GMA in reactive diluents due to the increasing epoxy ring in the mixture. EM3 containing 70% GMA had the highest adhesion strength of 3.34 MPa and 5.12 MPa for metal and concrete mixed with 0.3% hardener. Meanwhile, EM1 mixed with reactive diluents containing 30% GMA had the lowest adhesion strength of 2.6 MPa and 3.6 MPa for metal and concrete mixed with 0.3% hardener.

Table 5 The effect of reactive diluents composition on the adhesion of concrete and metal substrates.

| Sample code | E0 | | EM1 | | | EM2 | | | EM3 | | | |
|------------------------------|---------------|-------|------|-------|-------|------|-------|-------|-----|-------|-------|------|
| | Adhesion, MPa | | | | | | | | | | | |
| Epoxy: hardener ratios | 1:0.3 | 1:0.5 | 1:1 | 1:0.3 | 1:0.5 | 1:1 | 1:0.3 | 1:0.5 | 1:1 | 1:0.3 | 1:0.5 | 1:1 |
| Concrete | 3.33 | 2.82 | 2.45 | 3.6 | 3.12 | 2.58 | 3.91 | 3.4 | 3.1 | 5.12 | 4.58 | 4.35 |
| Metal | 2.19 | 1.51 | 1.93 | 2.6 | 2.3 | 2.1 | 2.72 | 2.53 | 2.4 | 3.34 | 2.86 | 2.7 |

3.4.3. Tensile strength and elongation at break

Tensile strength of both pure and modified epoxy resin (E0) with reactive diluents containing different amounts of GMA is shown in Figure 4. An increase in hardener ratio from 0.3 to 1.0 % correlates to higher tensile strength. Vidil *et al.* (2016) stated that this was attributed to the cross-linking between epoxy and hardener. Comparing epoxy E0 mixed with a hardener in the ratio of 1:0.3 had lower tensile strength than 1:1. For modified epoxy, namely EM1 – EM3, reactive diluents affected the tensile strength of the films. EM3 had the highest GMA content and maximum tensile strength of 65.3 MPa when mixed with the hardener ratio of 1:1, while EM1, with the lowest GMA content, had a minimum tensile strength of 57.2 MPa under the same condition. This disparity was due to the higher cross-linking observed in sample EM3 compared to EM1 (Huang *et al.*, 2017). Figure 4 shows that tensile strength increased with increasing viscosity due to the rise in molecular weight as well as the cross-link of epoxy mixture and hardener (Jie *et al.*, 2022).

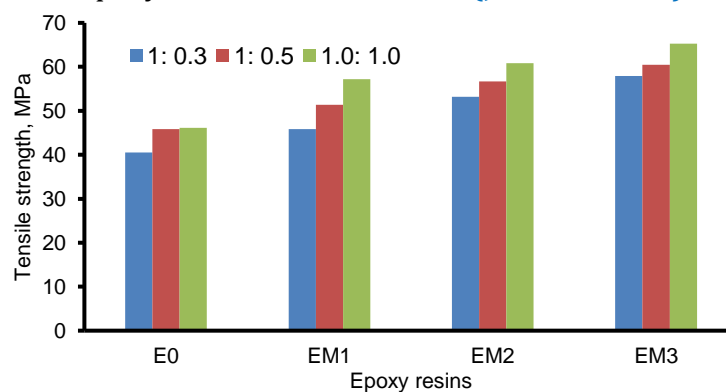


Figure 4 Tensile strength of pure epoxy (E0) and modified epoxies (EM1-EM3) at different hardener ratios

Figure 5 shows that the elongation at the break of pure and modified epoxy decreased with increasing hardener ratios and GMA content in reactive diluents due to side effects (Rahman *et al.*, 2012).

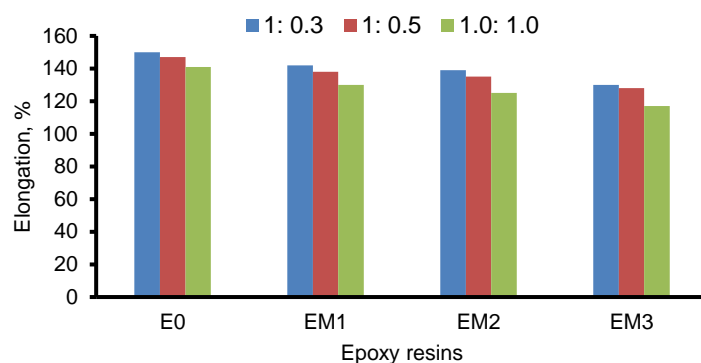


Figure 5 Elongation at break of pure epoxy (E0) and modified epoxies (EM1-EM3) at different hardener ratios.

3.4.4. Hardness

The effect of hardener ratio and GMA content in reactive diluents on the hardness of epoxy films is shown in Table 6. The hardness of epoxy films increased with increasing hardener ratios and GMA content in reactive diluents attributed to the rising cross-link between epoxy ring (epoxy resin & GMA) and hardener (Szewczak and Maciej, 2020). EM1 with 30% GMA content and a hardener ratio of 1:0.3 had a lower hardness (78) than EM3 containing 70% GMA and a hardener of 1:1. Generally, the hardness of epoxy films depended on different factors, including hardener ratios, diluent type, solvent, and concentrations (Ozeren and Ozkul, 2018; Syrmanova *et al.*, 2016; Villanueva *et al.*, 2009). Table 6 shows that increasing hardener ratios and GMA concentrations in reactive diluents enhanced the impact resistance and flexibility of cured epoxy-coated films.

Table 6 Mechanical properties of epoxy resin mixed with different reactive diluents.

| Sample code | E0 | | | EM1 | | | EM2 | | | EM3 | | |
|---------------------|-----------------------|-------|------|-------|-------|------|-------|-------|------|-------|-------|------|
| | Mechanical properties | | | | | | | | | | | |
| Epoxy: hardener | 1:0.3 | 1:0.5 | 1:1 | 1:0.3 | 1:0.5 | 1:1 | 1:0.3 | 1:0.5 | 1:1 | 1:0.3 | 1:0.5 | 1:1 |
| Impact test | P | P | F | F | P | P | F | P | P | P | P | P |
| Cylindrical Mandrel | P | F | F | P | P | F | P | P | P | P | P | P |
| Cross Hatch | p | F | F | P | P | F | P | P | P | P | P | P |
| Hardness | 75 | 79 | 80.5 | 78 | 79.5 | 81.9 | 84 | 86.9 | 88.7 | 85 | 86.5 | 89.6 |

4. Conclusions

In conclusion, Poly(St-co-GMA) copolymer, one of reactive diluents for epoxy resin, was successfully synthesized with various ratios of monomers (70:30, 50:50, and 30:70 w/w) using free the radical solution polymerization method to improve the physical and mechanical properties of epoxy resin in the presence of an amine-based hardener at ratios of 1:1, 1:0.5 and 1:0.3. The incorporation of GMA epoxy groups improved the adhesion of anticorrosion coatings, barrier properties, thermal stability, and service life. Meanwhile, mixed epoxy resins enhanced adhesion and tensile strength. Reactive diluents and hardener with ratios of 30:70 and 1:0.3 had the highest mechanical properties. The hardness of epoxy films, impact resistance, and flexibility increased with higher hardener ratios and GMA concentration in reactive diluents, enhancing mechanical and physical properties. The results provided insights into optimizing the solvents used in the coating industries, potentially changing it to solvent-free coatings with exceptional mechanical

properties and reduced environmental pollution. The knowledge and use of Poly(St-Co-GMA) for various epoxy resin applications improved further by these initiatives.

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