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# The Effect of Thermoplastic Polyurethane Addition on the Self-Healing of Polyester Primer Coating on Metal Substrate

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Corrosion can be prevented by extending the coating protection against the penetration of electrolyte formed from the corrosive environment. The incorporation of Thermoplastic Polyurethane (TPU) as self-healing agent into the Unsaturated Polyester (UPR) polymer can prolong the coating properties of the composite. UPR and TPU were prepared using mechanical mixing technique at various loadings of 10%, 20% and 30% weight of TPU. The mixture was added with curing agent, coated on steel plate and was left to cure. The coating was studied for adhesion, mechanical and corrosive properties using pencil hardness, adhesion tape and immersion tests. The incorporation of TPU regardless of weight % led to a reduction in mechanical properties from 2H grade to H grade. Nonetheless, there was an enhancement in adhesion post-healing with 20% TPU inclusion at 2B grade, indicating the 50% of healing efficiency. Result also recorded 45% of healing efficiency for corrosion rate in tafel polarization which was from 1.0768 to 0.5912 mmpy for the same TPU integration. The immersion results indicated the corrosion improved from 5G to 6G, demonstrating the recovery as supported by SEM images recorded at 58% of healing efficiency. Thus, it was concluded that 20 wt.% of loading TPU is an optimum loading percentage despite the reduction in mechanical and adhesion properties as it offers superior corrosion resistance compared to other loading percentages.

**Keywords**: Self-healing; thermoplastic polyurethane; polyester; primer coating; adhesion

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The self-healing approach is the material designed with the ability to repair for damages either autonomously or using stimuli [1]. The self-healing ability restores engineering performance upon damage, hence extending the lifespan of materials while reducing labour and replacement costs [2]. Recently, self-healing technology has gained significant attention from researchers in various industries such as construction, medical and corrosion protection. Several strategies have been applied to the self-healing coating, including polymer composites containing microcapsule, dynamic reversible chemistry, microvascular networks stored and inclusion of thermoplastic additives [3]. The stimuli for initiating a self-healing mechanism include mechanical, thermal, optical and also electrochemical stimuli. Despite the different stimuli and strategies, the process started with the occurrence of damage, and then the "mobile phase" is triggered either with or without stimuli, followed by the mass transport to the damage, especially in self-healing coating [4].

Self-healing coating is one of the important strategies that can enhance the coating performance against corrosion. The coating is a thin polymer layer deposited on a metal substrate to form a passive barrier to prevent corrosion by blocking direct contact between the metal and a corrosive environment [5]. Coatings are usually applied to metal substrates exposed to extreme conditions, such as structural metals in the oil and gas industry, making them prone to form cracks induced by mechanical forces [1]. The primer coating is the first layer applied to the metal substrate and acts as the final defence against corrosion [6]. The utilization of self-healing primer coatings is highly advantageous for corrosion protection. Spera et al. [7] used self-healing with the core-shell nanofiber that gave an immediate response of 97.5% initiated by the water that provided anti-corrosion protection of the substrate. Wang et al. [8] successfully developed the self-healing coating with the self-reporting ability using the microcapsule technique that can report the

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damage using 2′,7′-dichlorofluorescein (DCF). The dual function which is anti-corrosion protection with damage report was successfully embedded in the coating, resulting in a significant improvement [8]. Nevertheless, the microcapsule technique is challenging to produce and difficult to disperse within the composite system, hence restricting its application in the coatings [9]. According to the literature, engineering coatings are considered as mature and were unlikely to undergo significant changes in processing due to their highly optimized systems [3].

The intrinsic strategy is a simpler and more straightforward method in terms of preparation and processing, such as incorporating a thermoplastic additive into the coating system. Rodriguez et al. [10] employed the same shape memory-assisted self-healing (SMASH) concept into a similar chemical composition with a different fabrication method, blending polycaprolactone diol (PCL) with DGEBA to create polymerization-induced phase separation morphology. This technology has a comparable self-healing mechanism with only a one-step coating process. Yuan et al. [11] utilized the thermoplastic polyurethane (TPU) in the epoxy (DGEBA) coating system, where the reaction of PCL and isocyanate provides an improved processing window and mechanical properties, achievable by a simple blending procedure. Although the previous works simplify the chemistry and manufacturing procedures, the authors rarely discuss the engineering performance and processability of the resultant coatings, which is important for modern engineering applications. TPU is synthesized through the reaction of isocyanate, which contributes to enhanced mechanical properties, whilst diol, a long-chain soft polymer, acts as a mobile phase of the soft segment. The diol structure allows the reorganization of soft segments, facilitating the healing process. Polyester is a thermoset polymer is widely used as primer coating due to the ease of processing, low cost and durability. Nevertheless, polyester lacks of self-healing capabilities [12].

To overcome the absence of self-healing properties on the primer coatings, we explored the self-healing coating systems utilizing linear thermoplastics as the fusion phase in the polyester primer coatings. A series of TPU loadings (10%, 20%, and 30%) were employed with the polyester using a mechanical blending and subsequently applied to the metal substrate via brushing technique. The prepared primer coatings were tested for physico-mechanical testing using thickness and pencil hardness tests, while adhesion tests tape was used to ascertain the bonding strength. To ensure corrosion protection, the primer coatings on metal were subjected to immersion and tafel polarization before and after the healing process. The sample was characterized using Fourier Transform Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) imaging, and the self-healing mechanism was investigated.

## EXPERIMENTAL

### Chemicals and Materials

Unsaturated Polyester Resin (UPR, $C_4H_{10}O_2$, average Mn ~2000 g/mol with 40% styrene), Methyl Ethyl Ketone Peroxide (MEKP, $C_8H_{18}O_6$) and Cobalt (II) were purchased from Grunchem Tech Sdn Bhd, Malaysia. Polycaprolactone diol (PCL, $C_6H_{10}O_2$, average Mn ~2,000), 1,4-Phenyl diisocyanate (PPDI, $C_6H_4(NCO)_2$, average Mn 160.13 g/mol), and Maleic anhydride (MA, $C_4H_2O_3$) were acquired from Sigma Aldrich, USA.

### Methodology

For UPR-$TPU_{30}$, 1.5 g of TPU was weighed and mixed with 0.1 g MA in a vial bottle and served as a compatibilizer, as illustrated in **Figure 1**. The TPU and MA were melted at 90 °C for 30 min until a yellowish liquid was formed. Subsequently, 3.5 g of UPR was added into the solution and homogeneously mixed until there was no separation observed.

Next, the mixture was subjected to sonication for 5 min before being added with 0.5 mL MEKP and 0.25 mL of cobalt accelerator and agitated for an additional 1 min. Then, the mixture was coated to the metal substrates using hand brushing techniques in three layers. The sample was allowed to cure at room temperature for 7 days to ensure complete curing before characterization and testing. The procedures were repeated using 0.5 g and 1 g of TPU for UPR-$TPU_{10}$ and UPR-$TPU_{20}$, respectively, as shown in **Table 1**.

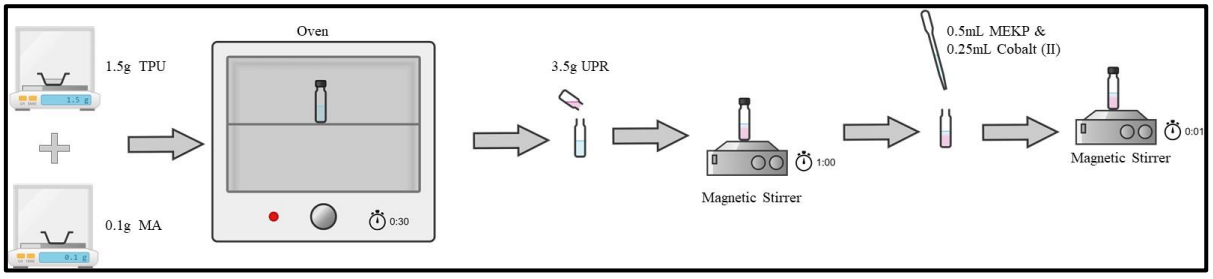



**Figure 1.** Schematic procedure of mixing UPR and TPU using mechanical blending method.

**Table 1.** Formulation used for each of the sample prepared.

| Sample | Formulation | Thermoplastic Polyurethane (g) | UPR (g) | Loading [%] |
|---|---|---|---|---|
| Sample 1 | Control | 0.0 | 5.0 | 0.0 |
| Sample 2 | UPR-$TPU_{10}$ | 0.5 | 4.5 | 10.0 |
| Sample 3 | UPR-$TPU_{20}$ | 1.0 | 4.0 | 20.0 |
| Sample 4 | UPR-$TPU_{30}$ | 1.5 | 3.5 | 30.0 |

**Physico-mechanical and Corrosion Testing**

The thickness measurement was carried out at 5 different spots on the coated metal substrate using Mitutoyo 547 Thickness Gauge. Pencil Hardness was performed using different pencil hardness from softest at 6B, 5B, 4B, 3B, 2B, HB, H, 2H, 3H, 4H, 5H and 6H; the hardest grades by ASTM D3363. The pencil was attached to the pencil hardness tester and pressed until a scratched mark of 6 mm length was formed on the coating. The adhesion test was conducted by scratching the coated sample in a 5 mm × 5 mm pattern on the coating. The sample was securely affixed using Scotch tape and allowed to rest for 1 min before being subjected to continuous pulling, with grading assessed according to ASTM D3359, where 0B represents the lowest grade, and 5B is the highest. The samples were subjected to corrosion testing by immersion in a 3.5% NaCl solution for 9 days. The samples were categorized based on the conditions before and after the healing process and graded following ASTM D610, where all the grades were illustrated in the Standard Practice for Evaluating the Degree of Rusting on Painted Steel Surfaces. Tafel polarization was carried out by immersing a coated steel plate with platinum foil and a saturated calomel electrode, which served as both the counter electrode and a reference electrode, via an Autolab PGSTAT204 in a 3.5% NaCl solution. The data was analysed using Nova 2.1.

**Characterization Methods**

ATR-FTIR was used to study the formation of TPU and its interaction with the optimum loading of UPR-$TPU_{20}$ compared to the control sample. The spectra used were ranged from 600 $cm^{-1}$ to 4,000 $cm^{-1}$. The sample initiated a self-healing process upon applying a heat stimulus to the scratch at 90 °C in an oven for 10 min to facilitate the healing of the coating. Scanning Electron Microscopy (SEM) was performed to enhance the morphological analysis of the self-healing recovery observed in all samples. All the samples were subjected to the healing process, and the healing efficiency was estimated according to the Equation (1) [13]:

$$\text{Healing efficiency} = (\sigma_{healed}/\sigma_{original}) \times 100\ \% \quad (1)$$

## RESULTS AND DISCUSSION

**Physico-mechanical**

Thickness is known as an important parameter for coating applications because it determines the separation between the metal and the corrosive environment [14]. The inconsistency in coating thickness may cause the protection coating system to fail, especially against corrosion. Based on the data recorded in **Table 2**, the overall thickness of the coating for all samples were in the range of 0.31 mm up to 0.33 mm. All measurements showed uniform thickness values, indicating the incorporating of TPU into the coating system did not affect the coating thickness. The result also indicated that the smooth surface was coated on the metal substrate with a margin of 0.01 between each coating. In addition, the presence of TPU in the UPR primer is well homogenized as there is no formation of agglomerates in the primer coating, resulting in uniform thickness measured [14].

**Table 2.** Thickness of the primer coating for control, UPR-$TPU_{10}$, UPR-$TPU_{20}$ and UPR-$TPU_{30}$.

| Samples | Thickness(mm) | | | | | |
|---|---|---|---|---|---|---|
| | 1st Reading | 2nd Reading | 3rd Reading | 4th Reading | 5th Reading | Average |
| Control | 0.29 | 0.32 | 0.35 | 0.28 | 0.31 | 0.31 |
| UPR-$TPU_{10}$ | 0.34 | 0.32 | 0.34 | 0.31 | 0.32 | 0.33 |
| UPR-$TPU_{20}$ | 0.34 | 0.32 | 0.31 | 0.35 | 0.32 | 0.32 |
| UPR-$TPU_{30}$ | 0.31 | 0.32 | 0.36 | 0.34 | 0.31 | 0.33 |

**Table 3.** Pencil hardness result (ASTM D3363) for control, UPR-$TPU_{10,}$ UPR-$TPU_{20}$ and UPR-$TPU_{30}$, before and after healing process.

| Sample | Before healing | After Healing |
|---|---|---|
| Control | 2H | 2H |
| UPR-$TPU_{10}$ | H | H |
| UPR-$TPU_{20}$ | H | HB |
| UPR-$TPU_{30}$ | HB | 2B |

Hardness plays a crucial parameter to evaluate the mechanical performance of coatings under external forces, particularly in coating applications. According to the data presented in **Table 3**, the control sample exhibited a 2H grade of pencil hardness both before and after the healing procedure. Incorporating TPU into the polyester primer reduced the hardness, with UPR-$TPU_{10}$ and UPR-$TPU_{20}$ were recorded at H grade before the healing process. For UPR-$TPU_{30,}$ the hardness decreased further to HB grade indicating a reduction in the coating's hardness. A similar trend was observed prior to the healing process, where higher TPU loadings reduced the hardness of the coating to HB grades. Precisely, UPR-TPU10 demonstrated H grade, while UPR-TPU20 and UPR-TPU30 exhibited HB and 2B grades, respectively.

The main factor influencing the reduction of hardness was the molecular structure and chain entanglement of TPU, as TPU polymers possess flexible, long-chain structures with both soft and hard segments, along with weaker intermolecular forces [15]. Additionally, the covalent bonding characteristic of TPU in the primer coating results in lower mechanical properties compared to UPR, which features crosslinked chain polymers and exhibits microphase separation [16]. TPU also exhibited a softer material, particularly with the inclusion of linear diol in the structure, which responded to heat during the healing process. The decrease in hardness following the healing process was noted due to the reorganization occurred on the coating's surface. The mobile phase from the diol in the TPU rearranged itself to fill any possible gaps and voids, predominantly exposing TPU on top of the coating. This contributed to the reduction in the coating hardness, with UPR-$TPU_{20}$ being 1 time softer while UPR-$TPU_{30}$ being 3 times softer. Although increasing TPU loading resulted in the reduction of coating hardness following healing treatment or heat exposure, the inclusion of TPU improved the flexibility by reducing the rigidity of the material. This condition is in good agreement with the adhesion values, as assessed both before and after the healing process.

The adhesion results in **Table 4** indicated that the control sample recorded the lowest grade at 0B, with approximately 65% of the coating detaching from the metal substrate. Similar results were recorded for the post-healing phase of the coating, indicating that heat did not exert any significant effect on the coating. The addition of TPU at 10 wt.% was recorded at 2B grade, with 15%-35% of the area removed from the substrate remaining unchanged before and after the healing process. However, increasing the TPU loading in the UPR primer coating reduced the adhesion grades to 1B and 0B for UPR-$TPU_{20}$ and UPR-$TPU_{30}$, respectively. These observations indicated that reducing the TPU content in the polyester primer reduced flaking and damage, possibly due to increased flexibility and decreased rigidity of the material. The damage observed in the primer coating was exposed to the applied forces during the scotch tape assessment. This damage concentrated stress on the coating, reducing the mechanical strength of the coating [17]. The results aligned well with the pencil hardness findings, indicating that higher TPU loadings reduced the adhesion grades. Apparently, while UPR-$TPU_{20}$ exhibited a comparable reduction in hardness, it also possessed good healing efficiency.

**Table 4.** Adhesion tape result (ASTM D3359) for control, UPR-$TPU_{10,}$ UPR-$TPU_{20}$ and UPR-$TPU_{30}$, before and after healing process.

| Sample | Before healing | After healing | Healing efficiency |
|---|---|---|---|
| Control | 0B \| >65% | 0B \| >65% | - |
| UPR-$TPU_{10}$ | 2B \| 15-35% | 2B \| 15-35% | - |
| UPR-$TPU_{20}$ | 1B \| 35%-65% | 2B\| 15-35% | 50% |
| UPR-$TPU_{30}$ | 0B \| >65% | 1B \| 35%-65% | 50% |

In the self-healing study of the primer coating, all samples experienced self-healing procedures upon scratches on the coating. The recorded results indicated no significant changes between the control and UPR-$TPU_{10}$ samples. Interestingly, UPR-$TPU_{20}$ and UPR-$TPU_{30}$ recorded improved adhesion test to 50% of healing efficiency. UPR-$TPU_{20}$ improved from 1B grade to 2B grade while UPR-$TPU_{30}$ improved from 0B grade to 1B grades. As mentioned earlier, the scratched area exposed the damaged coating area, allowing the TPU to realign and reconstruct, repairing the affected areas [11]. This recovery process reduced the stress concentration area, enhancing the adhesion strength between the coating and the substrates [5]. Hasniraaiman et al. [18] also reported that increased flexibility may lead to enhanced adhesion strength of the coating, resulting in better corrosion protection. Although the incorporation of TPU into the polyester primer reduced the hardness and the adhesion properties, the presence of TPU was able to recover the damage of the primer coating once being exposed to the stimuli, resulting in enhanced coating protection against corrosion as supported by the immersion and tafel polarization results.

**Corrosion Protection Properties**

The polarization resistance of the control sample was recorded at 334.23 Ω and 2.2935 mmpy in **Table 5** due to the neat polyester having high shrinkage, leading to the formation of the void contributed to the electrolyte pathway into metal substrates [19]. The high amorphous region from the styrene reduced the crystalline region, causing the easier pathway for electrolytes to pass through the coating. Meanwhile, the incorporation of TPU increased the polarization resistance and lowered the corrosion rate where UPR-$TPU_{10}$ was recorded at 2871.55 Ω and 1.3275 mmpy. The trend continued for the UPR-$TPU_{20}$ and UPR-$TPU_{30}$ where tafel polarization was recorded at 2496.18 Ω and 2516.23 Ω with 1.0768 mmpy and 0.9303 mmpy, respectively. TPU was produced by the reaction of PCL and PPDI which pre-dominantly consisted of diol in the main structure. Diol is known as a material that consists of long hydrocarbon chain that reacts non polar towards the water [20]. The incorporation of non-polar material into the primer coating disrupts or reroutes the electrolyte pathway in the coating [21]. An increase in TPU loading further reduces the corrosion rate by limiting the electrolyte path and increasing the non-polar behaviour of the coating.

The same sample was subjected to healing treatment prior to tafel polarization test to evaluate the healing efficiency of the coating as shown in **Figure 2**. It was recorded that UPR-$TPU_{10(heal)}$ had polarization resistance at 2561.17 Ω at 0.9203 mmpy of corrosion rate which was 30.39% lower corrosion rate as compared to the prior healing process. UPR-$TPU_{20(heal)}$ also recorded better corrosion protection at 2813.23 Ω of polarization resistance at 0.5912 mmpy of corrosion rate, indicating the 45.09% healing efficiency. Meanwhile, UPR-$TPU_{30(heal)}$ recorded the highest healing efficiency at 48.53% at 0.4726 mmpy of corrosion rate with 3118.84 Ω of polarization resistance. In summary, increasing the TPU loading enhances corrosion protection by reducing the corrosion rate and enhancing the healing efficiency. TPU acts as a barrier, filling the gaps and voids within the coating system, thereby enhancing the coating protection on the metal substrate towards the electrolyte. Overall, the tafel polarization results demonstrated in improved coating protection, attributed to the self-healing characteristics of the primer coating.

**Table 5.** Tafel polarization result for Control, UPR-$TPU_{10}$, UPR-$TPU_{20}$ and UPR-$TPU_{30}$, before and after healing process.

| Sample | Ecorr(V) | Icorr(A) | OCP (V) | Polarization Resistance (Ω) | Corrosion rate (mmpy) | Healing efficiency |
|---|---|---|---|---|---|---|
| Control | -0.3210 | 0.0000194 | -0.243 | 334.23 | 2.9352 | |
| UPR-$TPU_{10}$ | -0.2990 | 0.0000426 | -0.208 | 2871.55 | 1.3275 | - |
| UPR-$TPU_{20}$ | -0.2582 | 0.0000165 | -0.214 | 2496.18 | 1.0768 | - |
| UPR-$TPU_{30}$ | -0.2622 | 0.0000234 | -0.207 | 2516.23 | 0.9303 | - |
| UPR-$TPU_{10(heal)}$ | -0.2220 | 0.0000214 | -0.193 | 2613.17 | 0.9241 | 30.39% |
| UPR-$TPU_{20(heal)}$ | -0.2411 | 0.0000192 | -0.234 | 2813.23 | 0.5912 | 45.09% |
| UPR-$TPU_{30(heal)}$ | -0.2452 | 0.0000211 | -0.284 | 3118.84 | 0.4726 | 48.53% |

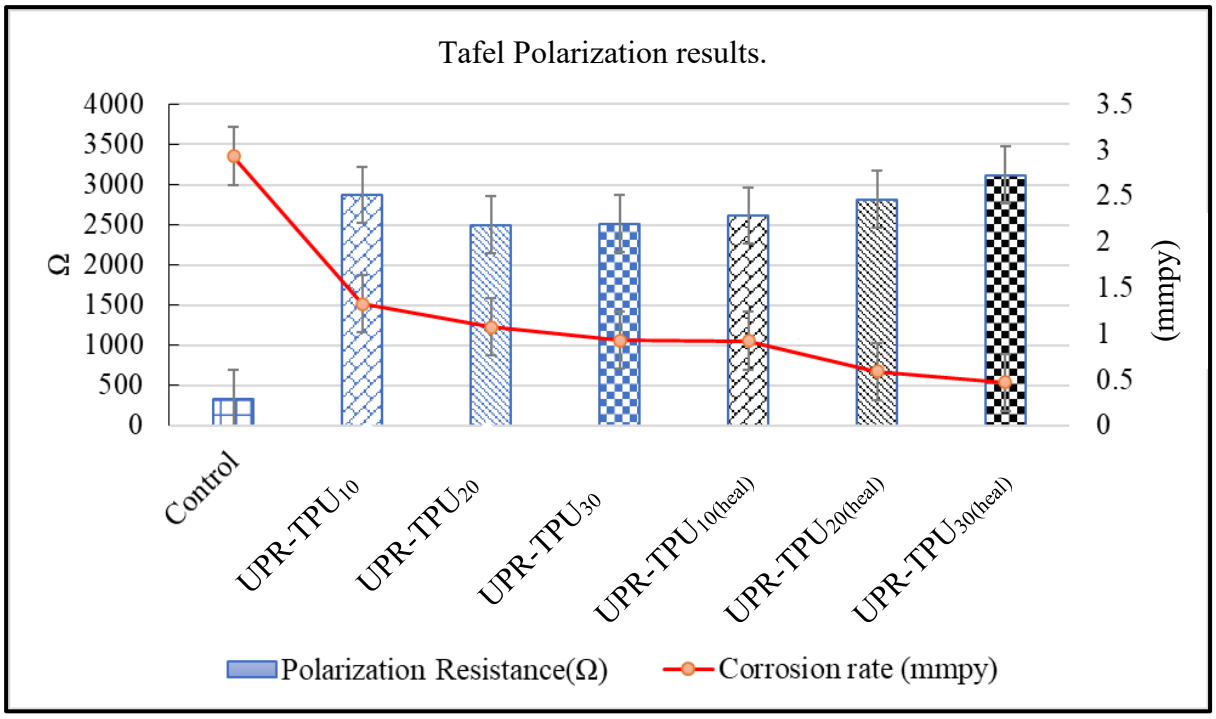



**Figure 2.** Tafel polarization result for Control, UPR-TPU$_{10}$, UPR-TPU$_{20}$ and UPR-TPU$_{30}$ for before and after healing process.

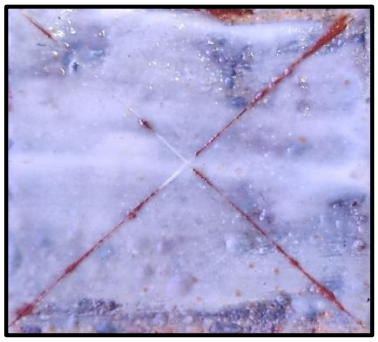
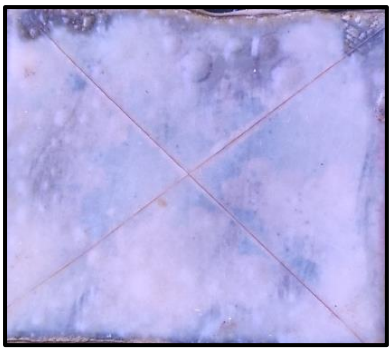
The immersion test was conducted on all samples to simulate the actual environmental conditions that were subjected to the failure of the primer coatings. All samples were immersed in 3.5% NaCl solution at a constant volume and monitored over a period of 9 days and the findings are tabulated in **Table 6**. The control sample was graded with 3G for both the pre- and post-healing samples. Both samples experienced the same corrosion process, with 16% of rusting. The corrosion grade for the UPR-TPU$_{10}$ dropped from 4G which indicated 10% rusting before the healing treatment, to 5G which indicated 3% rusting after the treatment, resulting in a healing efficiency of 20%. Following the healing process, the partial recovery of the scratched area was observed on the metal substrate. In the UPR-TPU$_{20}$, rust was detected at a lower rate of 3% at 5G, which improved to 1% at 6G following the healing procedure. At UPR-TPU$_{30}$ ,5G was recorded prior to healing and reduced to 7G, representing 0.3% post-healing nearly restoring the scratches on the metal substrate. Generally. the integration of TPU into the polyester primer has successfully imparted the healing capabilities of the coating. This is attributed to the presence of soft segment in the TPU, which allow the material to recover during the healing process and cover the X-scratch marks, as observed in the post-healing process. Heat stimulation transferred the energy to the soft segments, allowing the material to realign and flow as a mobile phase [22]. In addition, the shape memory and hydrogen bonding in the TPU facilitated the recovery, forming new bonds once the flow process was completed [23]. Phase separation within the primer coating also contributed to the healing process, preventing the penetration of the electrolyte into the coating and enhancing the coating's protective performance.

**The Study of Self-healing Mechanism with Illustration**

**Figure 3** illustrates the chemical structure of the UPR and TPU utilized as a primer coating. The TPU randomly distributed on the coating surface. The TPU was observed as a lighter colour in the coating as reported by Yu et al. [24], due to the formation of crystalline region by the PCL structure. In contrast, the low-contrast areas corresponded to the amorphous regions of the hard segment, as observed in the SEM imaging. The images revealed that microphase creation transpired in the polyester primer composite, facilitating the self-healing capability of the primer coating that enabled the recovery during the healing process. This microphase separation in the primer coating system caused a reduction of the physico-mechanical properties as reported earlier, and therefore allowed the self-healing capabilities of the primer coating. The hydrogen bonding of TPU reacts during the recovery of the bonding facilitating the attachment and detachment of the bonding between the hard phase region [1]. This also contributed to the reduction of its mechanical properties as reported in the hardness and pull-out tests. The addition of MA did not impact the coating properties since it was added with a very low amount and served as a compatibilizer. Hence, both microphase separation and the hydrogen bonding allowed the coating to recover, resulting in improved corrosion protection after the healing process. Enhanced self-healing is

generally observed in polymers that possess dynamic covalent bonds, microphase separation, and phase transition. The hard and soft segments of TPU enable the material to rearrange and close the cracks due to the mobility of the soft segments, particularly those cured at elevated temperature.

**Table 6.** Immersion result after 9 days of immersion for primer coating sample with and without the healing process.

| Sample | Before healing | After healing | Healing efficiency |
|---|---|---|---|
| Control |  3G (16% rust) |  3G (16% rust) | - |
| UPR-$TPU_{10}$ |  4G (10% rust) |  5G (3% rust) | 20% |
| UPR-$TPU_{20}$ |  5G (3% rust) |  6G (1% rust) | 20% |
| UPR-$TPU_{30}$ |  5G (3% rust) |  7G (0.3% rust) | 40% |

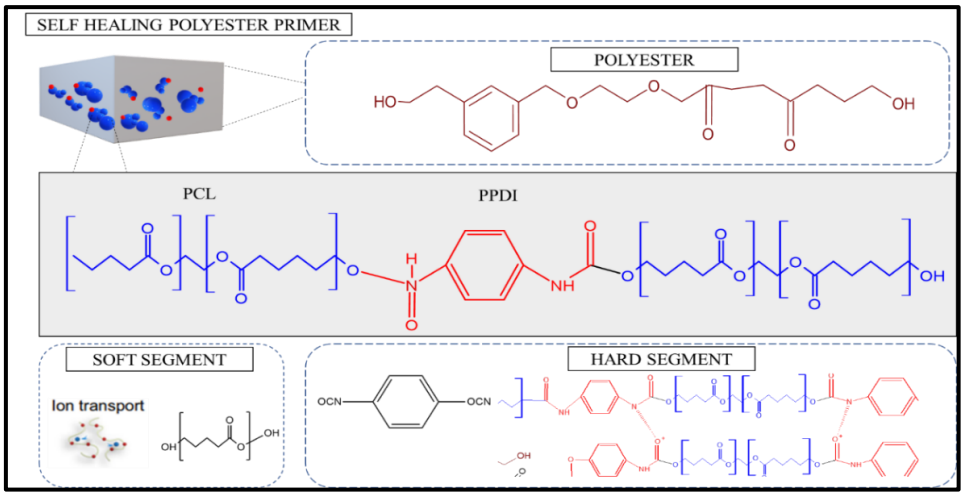



**Figure 3.** Chemical structure of UPR and TPU primer coating.

**Figure 4** illustrates the coating after being scratched and following the healing process. Upon the occurrence of a scratch, the TPU, with its lower mechanical strength compared to thermoset polyester, is more prone to bond breakdown. Hence, the incorporation of TPU with a high soft segment content imparts the mechanical properties of the overall primer coating. Simultaneously, the soft segment in the TPU polymer structure imparts flexibility to the coating, facilitated by the formation of the crystalline regions derived from the PCL properties. These crystalline regions allow the polymer structure to rearrange by increasing the chain mobility to recover the defect of the coating as shown in **Figure 4**. Thapa et al. [25] reported that PCL is capable of melting when exposed to temperatures ranging from 55 to 60 °C, corresponding to its melting point. The heat exposure at 90 °C during the healing process softened the soft segment of TPU to become semisolid and facilitated the recovery of the damaged area by filling the damaged area. This recovery successfully enhanced the protection of the metal substrates, contributing to a reduction in corrosion rate and rust rating, as observed in the immersion test results.

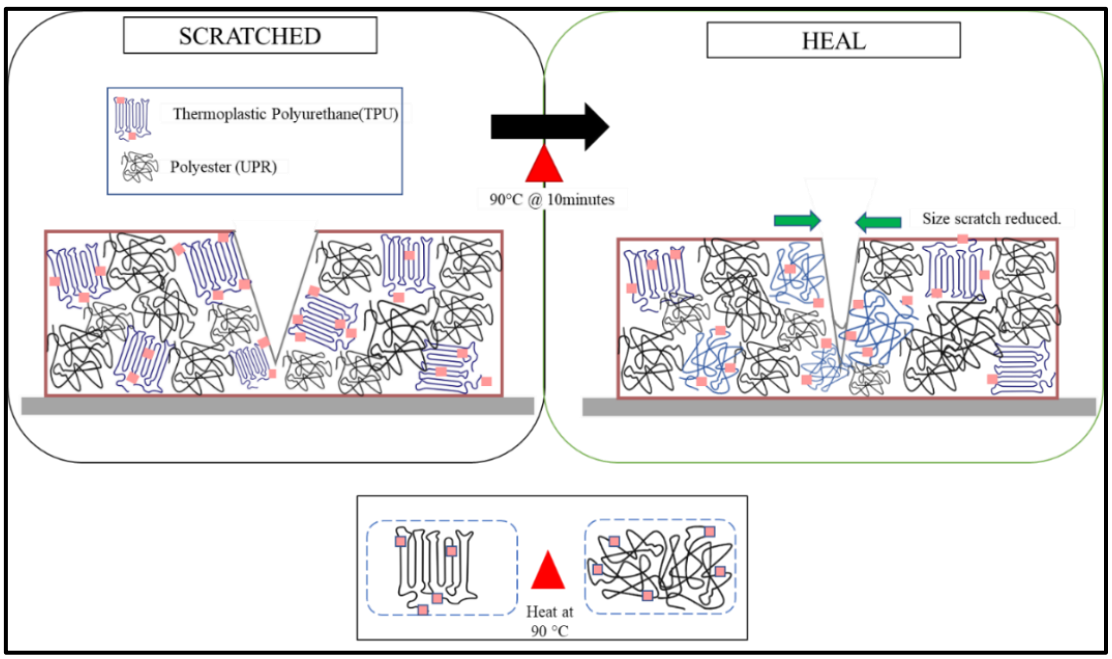



**Figure 4.** Study mechanism of self-healing polyester primer coating.

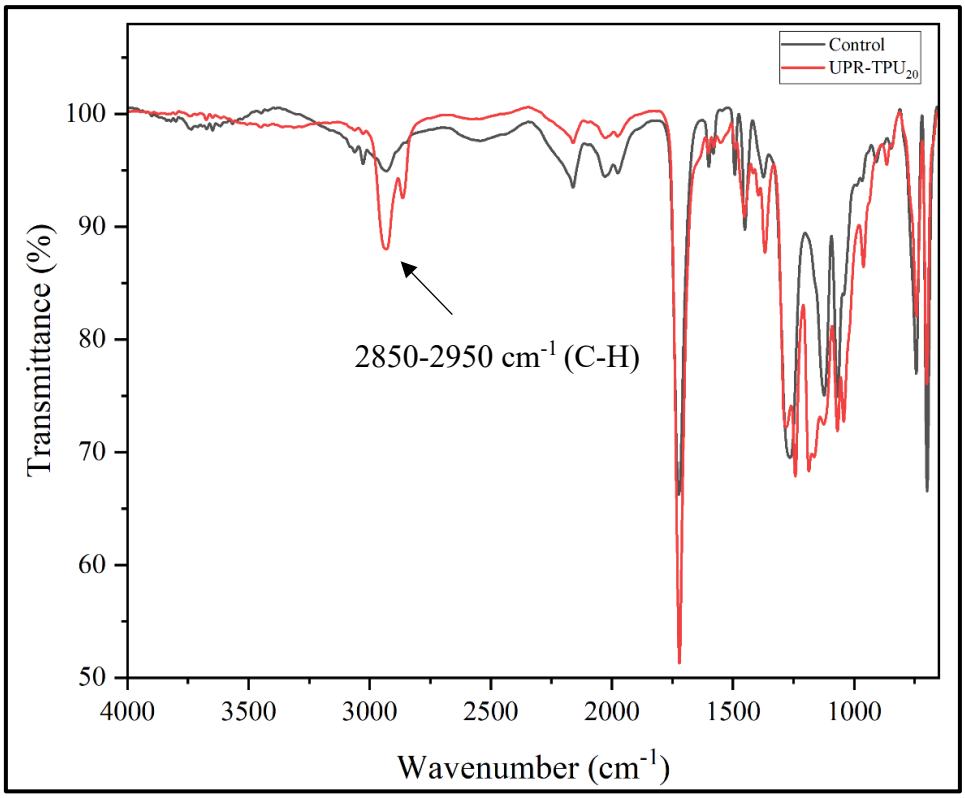



**Figure 5.** The FTIR spectrum for control and the UPR-$TPU_{20}$.

**FTIR Analysis**

FTIR was used to study the interaction between the polyester primer coating and the optimized addition of the TPU in the coating system as shown in **Figure 5**. Based on the spectrum, the peak was observed at 1720 $cm^{-1}$ (C=O stretching) and 1240–1260 $cm^{-1}$ (C-O stretching), indicating the polyester coating in the control sample [26]. The incorporation of TPU into the coating system was observed at peak 1500–1600 $cm^{-1}$ (N-H bending), indicating the presence of isocyanates in the structure [27]. There was an increased intensity at peak 1650–1700 $cm^{-1}$ and 2850–2950 $cm^{-1}$, implying the C-H bending and C-H stretching, respectively in the primer system. This improvement was attributed to the presence of the soft segment of TPU, which enhanced corrosion protection and facilitated the recovery of the coating [28]. Additionally, the C-H chain is hydrophobic in nature, which contributed to enhancing the protective properties of the primer coating [5].

**SEM Imaging**

SEM analysis was carried out to observe the recovery of the primer coating after the self-healing treatment. The coating was scraped with a scratch maker to simulate damage before undergoing the healing procedure at the same location. **Figure 6(a)** reveals a distinct scratch, indicating penetration through the coating. Meanwhile, **Figure 6(c)** illustrates the post healing phase at the same magnification employed. Changes in the scratches precisely on the appearance of the coating were observed. The light colour of the scratch area signifies the change in depth, indicating that the scratch did not penetrate farther, therefore suggesting recuperation has taken place [28]. This finding is in line with the recovery and the reduction of the corrosion rate in the immersion and the tafel polarization tests. The magnification was increased to 1000 times in **Figure 6(b)** and **6(d)** for the pre- and post-healing stages, respectively. The scratch's gap was measured and tabulated in **Table 7**. The average distance of the scratch was 47.40 µm for pre-healing sample while post healing process recorded the average distance was 19.80 µm, indicating 58.23% of healing efficiency. This reduction was attributed to the reconstruction of the soft segment in the TPU, which reconstructed the damage during the healing process. The calculated reduction of the scratch distance confirmed the effectiveness of self-healing in enhancing corrosion protection and aligned with the previous immersion results.

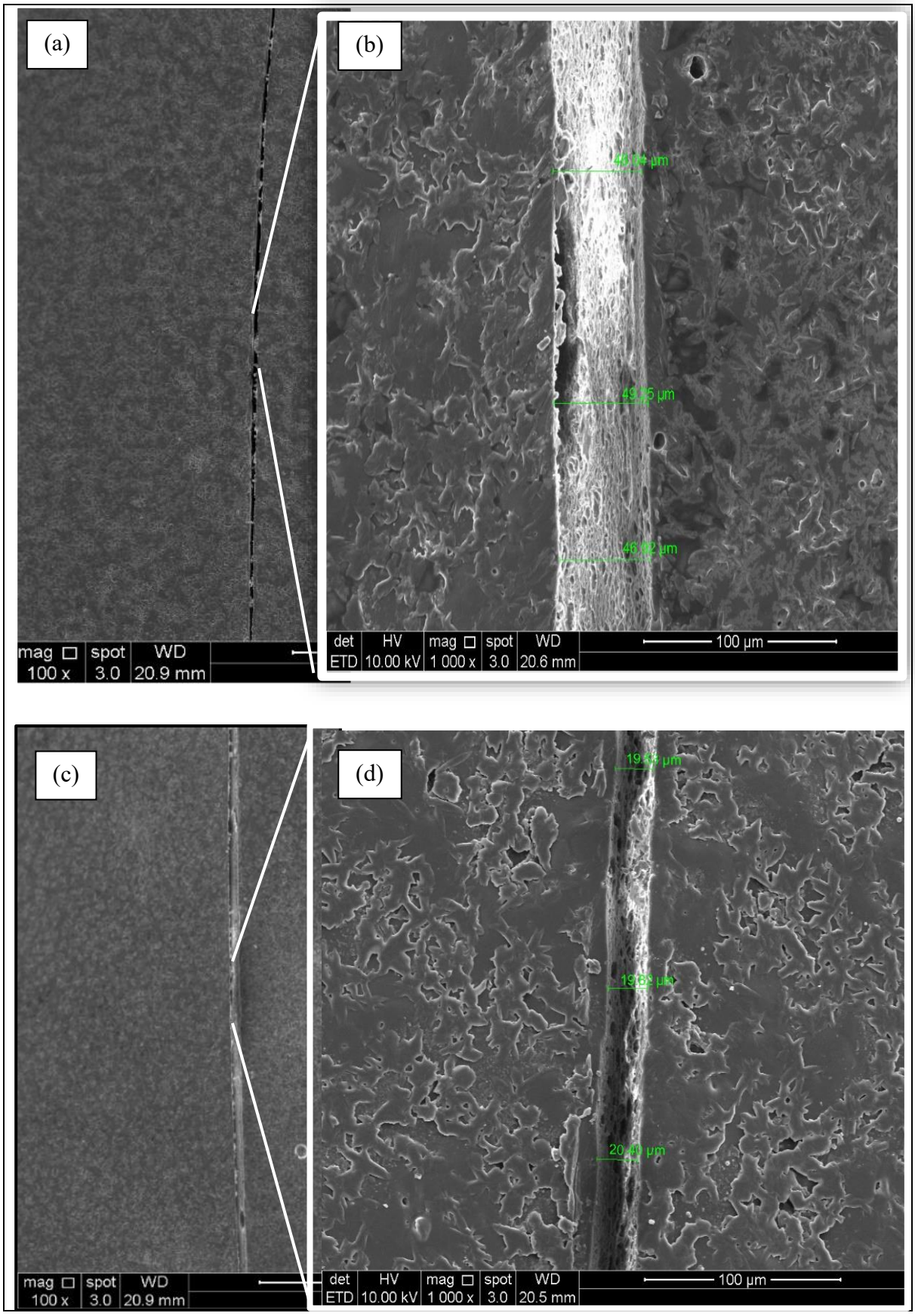



**Figure 6.** SEM imaging of (a) UPR-$TPU_{20}$ before healing at 100× magnification, (b) UPR-$TPU_{20}$ before healing at 1000× magnification, (c) UPR-$TPU_{20}$ after healing at 100× magnification, and (d) UPR-$TPU_{20}$ after healing at 1000× magnification.

**Table 7.** Scratch size before and after the healing process for UPR-$TPU_{20}$.

| Sample | Scratch Distance (μm) | | | | | | Healing efficiency |
|---|---|---|---|---|---|---|---|
| | Before healing | | | After healing | | | |
| UPR-$TPU_{20}$ | 46.04 | 49.25 | 46.92 | 19.53 | 19.82 | 20.40 | - |
| | Average: | | 47.40 | Average: | | 19.80 | 58.23% |

## CONCLUSION

In conclusion, self-healing properties are promising technologies for protective coatings due to their distinguished ability to recover and prevent corrosion, as successfully proven in this study. The incorporation of TPU self-healing agent in the polyester primer coating showed a prominent effect on self-healing and corrosion protection. UPR-$TPU_{20}$ was recorded as having a moderate reduction of hardness at H grade and 1B grade of the adhesion tape test. However, there was an improvement in adhesion after the healing process, which was recorded at 2B grade, with 50% healing efficiency. The healing efficiency for corrosion rate in tafel polarization was also recorded at 45.09%, which was from 1.0768 to 0.5912 mmpy. The immersion results indicated that the rust level improved from 5G to 6G, demonstrating a recovery assessed using SEM imaging, which recorded a healing efficiency of 58.23%. At 20% of TPU inclusion, it improved the self-healing ability of the polyester primer coating to recover and protect against corrosion. Tailoring the optimum loading of TPU at 20% improved the adhesion properties along with the self-healing ability.

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## REFERENCES

1. Zhang, Z., Rong, M. Z. and Zhang, M. Q. (2023) Self-healable functional polymers and polymer-based composites. *Progress Polymer Sciences*, **144**, 101724.

2. Ratwani, C. R. Kamali, A. R. and Abdelkader, A. M. (2023) Self-healing by Diels-Alder cycloaddition in advanced functional polymers: A review. *Progress Material Sciences*, **131**, 12, 101001.

3. Yuan, D., Bonab, V. S., Patel, A., Yilmaz, T., Gross, R. A. and Manas-Zloczower, I. (2020) Design strategy for self-healing epoxy coatings. *Coatings*, **10**, 1, 1–11.

4. Xie, J., Fan, L., Yao, D., Su, F., Mu, Z. and Zheng, Y. (2022) Ultra-robust, self-healable and recyclable polyurethane elastomer via a combination of hydrogen bonds, dynamic chemistry, and microphase separation. *Material Today Chemistry*, **23**, 100708.

5. Croll, S. G. (2020) Surface roughness profile and its effect on coating adhesion and corrosion protection: A review. *Progress Organic Coatings*, **148**, 105847.

6. Baharudin, A., Ahmad, Z., Sarip, M. N., Musa, L., Mohd Ishak, M. A., Abd Aziz, A. and Onn, M. (2023) Study of unsaturated polyester primer reinforced by microcrystalline cellulose on mechanical, adhesion and corrosion properties. *Materials Science Forum*, **1087**, 35–39.

7. Spera, N. C., Salazar-Castro, C., Álvarez de Eulate, P. C., Kolenko, Y. V. and Sousa, J. P. (2024) Self–healing core–shell nanofibers for corrosion protective coatings for offshore structures. *Progress Organic Coatings*, **191**, 108424.

8. Wang, Y., Wang, J., Huang, L., Ding, X., Chen, Z., Ren, C. and Zhang, D. (2023) Photothermally activated self-healing coatings for corrosion protection: A review. *Progress in Organic Coatings*, **185**, 107886.

9. Hia, I. L., Vahedi, V. and Pasbakhsh, P. (2016) Self-healing polymer composites: prospects, challenges, and applications. *Polymer Reviews*, **56(2)**, 225–261.

10. Rodriguez, E. D., Luo, X. and Mather, P. T. (2011) Linear/network poly(ε-caprolactone) blends exhibiting shape memory assisted self-healing (SMASH). *ACS Applied Material Interfaces*, **3**, 2, 152–161.

11. Yuan, D., Bonab, V. S., Patel, A. and Manas-Zloczower, I. (2018) Self-healing epoxy coatings with enhanced properties and facile processability. *Polymer (Guildf)*, **147**,196–201.

12. Abral, H., Fajrul, R., Mahardika, M., Handayani, D., Sugiarti, E., Muslimin, A. N. and Rosanti, S. D. (2020) Improving impact, tensile and thermal properties of thermoset unsaturated polyester via mixing with thermoset vinyl ester and methyl methacrylate. *Polymer Testing*, **81**, 106193.

13. Guadagno, L., Raimondo, M., Naddeo, C., Vertuccio, L., Russo, S., Iannuzzo, G. and Calabrese, E. (2022) Rheological, thermal and mechanical characterization of toughened self-healing supramolecular resins, based on hydrogen bonding. *Nanomaterials*, **12(23)**, 4322.

14. Asemani, H. R., Luo, L. and Mannari, V. (2020) Corrosion-resistant organic-inorganic hybrid pretreatments obtained by UV-initiated process suitable for primer-less coating systems. *Progress Organic Coatings*, **147**, 105878.

15. Sabahi, N., Roohani, I., Wang, C. H., Farajzadeh, E. and Li, X. (2023) Thermoplastic polyurethane-based shape memory polymers with potential biomedical application: The effect of TPU soft-segment on shape memory effect and cytocompatibility. *Polymer*, **283**, 126189.

16. Qu, Q., Wang, H., He, J., Qin, T., Da, Y. and Tian, X. (2020) Analysis of the microphase structure and performance of self-healing polyurethanes containing dynamic disulfide bonds. *Soft Matter*, **16**, 39, 9128–9139.

17. Klenam, D. E. P., McBagonluri, F., Bamisaye, O. S., Asumadu, T. K., Ankah, N. K., Bodunrin, M. O. and Soboyejo, W. O. (2024) Corrosion resistant materials in high-pressure high-temperature oil wells: an overview and potential application of complex concentrated alloys. *Engineering Failure Analysis*, **107920**.

18. Hasniraaiman, A. H., Zuliahani, A., Ishak, M. A. M., Faiza, M. A. and Azniwati, A. A. (2019) Comparison studies on corrosive properties of polyester filled graphene primer coatings via sonication and mechanical method. *Progress colour, colour & Coatings*, **12**, 4, 211–218.

19. Yeo, J. S., Lee, J. H. and Hwang, S. H. (2017) Effects of lignin on the volume shrinkage and mechanical properties of a styrene/unsaturated polyester/lignin ternary composite system. *Composite Part B: Engineering*, **130**, 167–173.

20. Naheed, S., Zuber, M., Barikani, M. and Salman, M. (2021) Materials Science & Engineering B Molecular engineering and morphology of polyurethane elastomers containing various molecular weight of macrodiol. *Material Science and Engineering:B*, **264**, 114960.

21. Wu, C. Wang, J., Lan, M., Wang, Z. and Wang, Z. (2023) Thermoplastic polyurethane film performance improvement by incorporation of furfuryl alcohol and polydimethylsiloxane. *Progress Organic Coatings*, **177**, 107429.

22. Wu, H., Xie, H., Tian, X., Sun, Y., Shi, B., Zhou, Y. and Yang, Y. (2021) Hard, tough and fast self-healing thermoplastic polyurethane. *Progress in Organic Coatings*, **159**, 106409.

23. Mouren, A. and Avérous, L. (2023) Aromatic thermoplastic polyurethanes synthesized from different potential sustainable resources. *European Polymer Journal*, **197**, 112338.

24. Yu, P., Huang, S., Yang, Z., Liu, T., Qilin, Z., Feng, J. and Zeng, B. (2023) Biomechanical properties of a customizable TPU/PCL blended esophageal stent fabricated by 3D printing. *Materials Today Communications*, **34**, 105196.

25. Thapa, M., Jony, B., Mulani, S. B. and Roy, S. (2019) Experimental characterization of shape memory polymer enhanced thermoplastic self-healing carbon/epoxy composites. *AIAA SciTech 2019 Forum*, **1112**.

26. Mohammadloo, A. E., Khorasani, M., Mohammadloo, H. E., Roshan, S., Ghamsarizade, R. and Sarabi, A. A. (2023) Dispersion stability, adhesion strength, and anti-corrosion properties of water-born polyester resins. *Materials Chemistry and Physics*, **301**, 127599.

27. Wu, H., Sheng, D., Liu, X., Zhou, Y., Dong, L., Ji, F. and Yang, Y. (2020) NIR induced self-healing polyurethane/polypyrrole nanocomposites. *Polymer*, **189**, 122181.

28. Wu, H., Xie, H., Tian, X., Sun, Y., Shi, B., Zhou, Y. and Yang, Y. (2021) Hard, tough and fast self-healing thermoplastic polyurethane. *Progress in Organic Coatings*, **159**, 106409.