

Research article

Investigation of the mechanical, tribological and corrosive properties of epoxy composite coatings reinforced with recycled waste tire products

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Abstract. The present work aims at evaluating the mechanical and anti-corrosion behaviour of epoxy coatings modified by recycled waste tire products. In this study, the epoxy coatings reinforced with ground tire rubber (GTR), devulcanised ground tire rubber (DGTR), pyrolytic carbon black (PCB) and original carbon black (CB) particle contents were prepared and applied to the galvanised steel substrate. Micro-mechanical tests (nanohardness and microscratch) were used to measure the mechanical properties of the coatings. Tribological and corrosive performance of the coatings were evaluated using reciprocating ball-on disc test and salt spray corrosion test (5 wt% NaCl), respectively. The experimental results showed that the recycled waste tire products reinforced composite coatings significantly improved resistance to wear and corrosion inhibition property. In the study, the most remarkable results were the increase in wear resistance by 77.7% in the coating strengthened with DGTR. The highest corrosion resistance was obtained in the epoxy coating reinforced with PCB, no white rust was observed on the coating during the salt spray test (1000 hours), and the lowest blistering degree of the sample after the test was obtained as 8F.

Keywords: polymer composites, coatings, devulcanised rubber, pyrolytic carbon black, tribological properties

1. Introduction

Recycling and reuse of waste tires are extremely important. The large amount of waste and the resulting environmental effects make recycling inevitable. Because of the three-dimensional structure network of rubbers, recycling is a current technological challenge. Today, the main end-of-life routes of tires are landfilling, incineration and grinding. But these methods show that there is no sustainable recycling of this valuable waste material. For this reason, it is much more important to recycle waste tires as materials by methods such as pyrolysis and devulcanisation, apart from direct evaluation methods. Recycled waste tires by these methods are actually an important source of raw materials with their recycling forms; devulcanised rubber, pyrolytic carbon black and pyrolytic

oil etc. If the properties of devulcanised rubber are sufficient, it can be used alone or by adding to a rubber recipe in various proportions [1]. Pyrolytic products can similarly be used in rubber recipes or in different areas such as fuels because they have high calorific value [2–4]. Various researchers have reported the application of ground tire rubber (GTR) particles as filler in thermoplastics and thermoset polymers [5–9]. In the literature, it has been seen that most of the studies on GTR particles filled thermoset resins related to the production and characterisation of bulk composite materials [6, 10–15]. However, the number of studies on adding GTR to coatings applied to metallic surfaces, which is an important area of use of thermoset plastics such as epoxy, is extremely limited.

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Metallic surfaces must be protected against both mechanical and corrosive effects. Metallic and polymeric coatings are commonly used for this purpose. Polymeric coatings can be applied directly to a metal surface or onto a metallic coating such as galvanised coatings. Second coating systems, called duplex coatings, give excellent mechanical and corrosive properties and may have an extremely long life with a minimum of maintenance [16]. Epoxy resins are well known to have good properties for coating metal surfaces. However, their mechanical characteristics, such as; ready brittleness, poor wear resistance, low fracture resistance and poor crack resistance, are insufficient to meet the variety of applications [17, 18]. Therefore, modification of epoxy resins is required to improve their properties. An effective approach is to add reinforcing particles to such polymers, including silica [19, 20], ZnO [19, 21], TiO₂ [22] and carbon forms (CNT, GO) [23–27]. As mentioned above, there is insufficient data on epoxy coatings reinforced with GTR particles concerning its effects on the coating properties. Adesina *et al.* [28] evaluated the effect of adding micronised GTR at different loading rates (1, 5, 10, 15 and 20 wt%) on the wear resistance of the epoxy coatings. They suggested that low loading of no more than 10% by weight is appropriate for reinforcing epoxy resin. They stated that increasing GTR loading causes deterioration of mechanical properties and wear resistance properties due to weak interfacial interaction, an increase of voids and the formation of a blend instead of a composite. In addition, the number of studies in which not only GTR particles but also devulcanised ground tire rubber (DGTR) and pyrolysis products are included in epoxy resin is extremely low. Aoudia *et al.* [29] used microwave devulcanised and non-devulcanised GTR particles as reinforcement in an epoxy matrix and characterised the mechanical properties of the obtained composites. It has been reported that as a result of microwave devulcanisation, DGTR-filled epoxy composites have better mechanical properties than those filled with GTR at the same loading

due to increased DGTR/epoxy adhesion. In the limited number of previous studies, each product was handled separately and not used in the same study, except for the study of Aoudia *et al.* [29] (GTR and DGTR). Therefore, more work is needed to understand the interaction between recycled waste tire products and epoxy matrix for the coating applications.

In this study, it was aimed to develop new composite coatings by adding recycled waste tire products (GTR, DGTR, PCB, CB) to the epoxy matrix, thus both finding new usage areas for waste tire products and improving the properties of epoxy. Cross-cut, hardness, scratch and wear tests were used to evaluate the mechanical and tribological performance of the particle-reinforced composite coatings. Coated test plates also stood in salt solution in order to determine the corrosion resistance. In addition, thermal stabilities of the composite coatings, the matrix-particle interactions, particle dispersions in the epoxy matrix and the wear surfaces were analysed using various methods.

2. Materials and methods

2.1. Materials

The epoxy resin based on bisphenol A (Polires 188; 182–192 g/epoxy equivalent) and phenalkamine-based hardener (Cardolite NC-562) used in this study were obtained from Polikem, Turkey. The ground tire rubber (GTR) obtained by grinding the tread and sidewalls of waste tires under ambient conditions was supplied from Unsal Kaucuk, Turkey. The devulcanised waste tire was obtained by microwave devulcanisation using the parameters detailed in our previous study (magnetron power: 800 W, exposure time: 5 min) [1]. The characteristics of the GTR and DGTR are given in Table 1. SEM photos of the GTR and DGTR are shown in Figure 1.

Pyrolytic carbon black (PCB) used in this study was supplied by a local tire pyrolysis plant (Tam Rubber, Turkey). The PCB was produced from the used tires using a fixed bed reactor at a temperature of 500–550 °C in the supplying plant. The PCB was used as

Table 1. Characteristics of GTR, DGTR, PCB and CB [2].

	Particle size	Specific surface area [m ² /g]	Ash [%]	Polymer type	Polymer ratio	Sulfur [%]	C [%]
GTR	<45 µm	0.017	12.59	NR/SBR	78/22	–	–
DGTR	<45 µm	0.295	23.78	NR/SBR	75/25	–	–
PCB	<45 µm	30.4	15.36	–	–	1.45	79.15
CB (N550)	45 nm	42.0	0.20	–	–	0.50	92.36

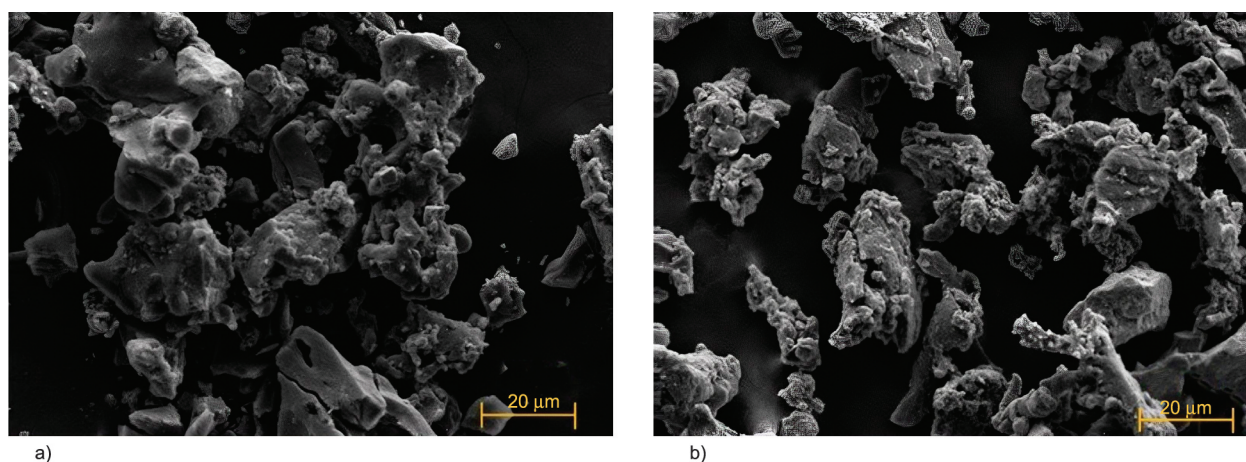


Figure 1. SEM photographs of a) GTR and b) DGTR (Magnification: 500×).

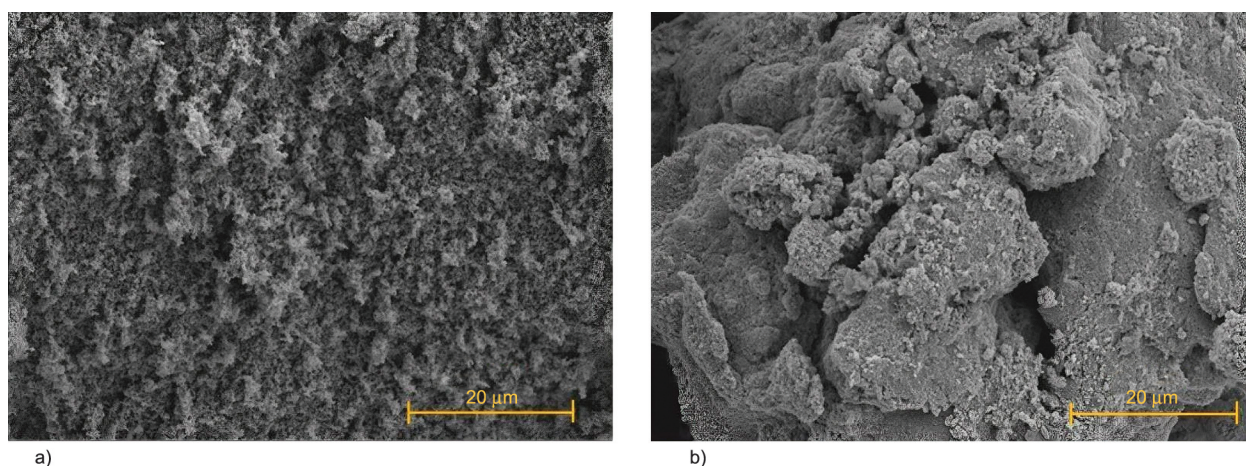


Figure 2. SEM photographs of a) N550 and b) PCB (Magnification: 5000×).

a filler in this study without removing ash or any other purification. The original carbon black (CB, N550) used in this study was supplied by Tupras, Turkey. The characteristics of the PCB produced by the tire pyrolysis plant are given in Table 1. SEM photos of CB and PCB are shown in Figure 2.

Galvanised steel plates (150×100×2 mm, 25×25×3 mm) were used as metallic substrates (Mysilo Co., Turkey). The galvanised steel plates had a zinc coating weight of approximately 350 g/m² and a thickness of approximately 30 µm. The galvanised steel plates were cleaned with acetone (Merck, Germany) and dried completely before applying the coating to increase the adhesion of the coating to the galvanised steel substrate.

2.2. Preparation of the composite coatings

Epoxy composite coatings containing three kinds of fillers, viz. GTR (3 wt%), DGTR (3 wt%), CB (3 wt%) and PCB (3 wt%) were prepared by the following procedures. In the first stage, after the particles were mixed with acetone, this mixture was

added to the epoxy resin, and then the mixture was mechanically mixed for 10 min with the laboratory-scale stirrer (Tops MS3040, Misung Scientific Co., Seoul, Korea). The mixture was kept in a vacuum oven (for 10 min, at -0.75 bar, Nüve Ev 018, Ankara, Turkey) to take out acetone and remove the air bubbles trapped inside. In the second stage, the hardener was added to the mixture, and the final mixture was mechanically mixed for 5 min. Finally, a film applicator (TQC LH 20/60, Netherlands) was used to deposit the neat epoxy (NE) and the composite coatings on the galvanised steel substrates (120 µm). All the coated steel plates were cooled at room temperature for 24 h and then post-cured at 80 °C for 2 h. Dry coating thickness was measured using dry film thickness instrument (Time TT-260, Time Co., China), and the average value of the coating thickness was found to be in the range of 110±10 µm. The samples were labelled according to the type of recycled waste tire products as EGTR, EDGTR, ECB and EPCB for GTR, DGTR, CB and PCB, respectively.

2.3. Characterisation

The epoxy matrix-particle interactions and the thermal stabilities of the composite coatings were characterised using Fourier transform infrared (FTIR, wavelength range: 500–4000 cm^{-1} , Perkin Elmer Spectrum 100, USA) and thermogravimetric (TGA, Heating rate: 10 $^{\circ}\text{C}/\text{min}$; Temperature range: 25–800 $^{\circ}\text{C}$, Exstar SII TG/DTA 7300, Hitachi High-Tech Science Co., Japan) analysis, respectively.

The adhesion strength of the coatings to the steel substrate was examined according to ASTM D 3359 standard using a cross-cut tape test.

Micro-mechanical tests, including nanohardness and microscratch tests were applied to determine the hardness and scratch-resistance of the composite coatings. The hardness of the coatings was tested using a nanoindentation tester with a Berkovich indenter (NHT2, CSM Instruments, Switzerland). During the test, a load was applied up to the maximum value of 20 mN, which was determined to be perpendicular to the sample surface using the penetrating tip, and after reaching this maximum load value, a gradual restoration was performed. The load [mN] – Depth [nm] curves obtained as a result of the test were analysed, and the hardness and elasticity modulus values of the coating samples were determined. The scratch-resistance of the samples was measured using the continuous load increase method up to 5 N with a Rockwell indenter (Diamond, 100 μm radius). Penetration depth, remaining depth and elastic recovery were measured in the samples under load.

To determine the tribological properties of the coatings, we performed a wear test using a ball-on-disc type reciprocating tribometer (CSM Instruments, Switzerland). The tests were conducted in an atmospheric environment, using a 6 mm diameter 440C stainless steel ball, under a load of 5 N, at 20 cm/s sliding speed and a total sliding distance of 300 m. The wear track was analysed to determine the wear depth and width using the 3D profiles of the Veeco Dektak-8 profilometer (Veeco Inc., USA). Surface roughness of composite coatings was also observed using the profilometer. Morphology of the wear tracks was analysed using a scanning electron microscope (SEM).

The corrosion protection performance of the coated plates was evaluated using salt spray corrosion test (ASTM B 117). The plates (with x-scratches) used in the salt test were placed in the temperature-controlled chamber (ASLI M300, ASLI Test Equipment Co.,

China) and were observed for 1000 hours (42 days). The solution used in the experiment is 5% by weight sodium chloride (NaCl, Safir, 99.7%, Turkey), spraying pressure is 0.9–1 bar and at a temperature of 35 ± 2 $^{\circ}\text{C}$. After this test, the size and frequency of blisters of the coatings are analysed according to ASTM D-714-87/00 (TS 9260 EN ISO 4628).

The morphology of the particle dispersion in the epoxy matrix, the particle-matrix interaction and the wear surface were studied using a scanning electron microscope (SEM, ZEISS EVO LS 10 Zeiss, Germany).

3. Results and discussions

3.1. FTIR and TGA Results

Figure 3 shows the FTIR spectra of the neat epoxy and the composites. Characteristic peaks for the neat epoxy resin are identified. With the addition of GTR, DGTR, CB and PCB particles, minor effects on functional groups can be seen in composite coatings. No significant difference in the peak intensities of the neat epoxy and both EDGTR and EPCB samples was observed. However, in comparison with the neat epoxy, a new peak was observed in the EGTR and ECB. The peak at 1724 cm^{-1} is assigned to the presence of a small amount of C=O groups [28, 30]. For the EGTR and the ECB, the observation of a peak at a wavelength of 1724 cm^{-1} can be attributed to the presence of oxidation and acidic groups [31] on the GTR and CB particle surfaces. Zedler *et al.* [32] stated that this peak seen in GTR occurred as a result of oxidative degradation during the grinding of the tire. TGA results are shown in Figure 4 and Table 2. It was observed that the temperatures slightly decreased at 5 and 50% weight loss with the addition of particles. The thermal degradation behaviour of epoxy composites was slightly affected by the addition of particles. The remaining weight of the coatings at

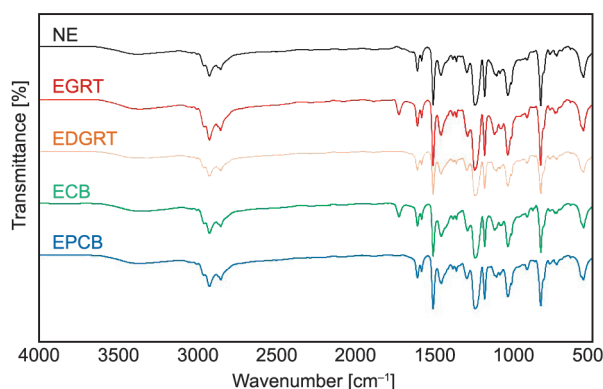


Figure 3. FTIR spectra of the neat epoxy and the composites.

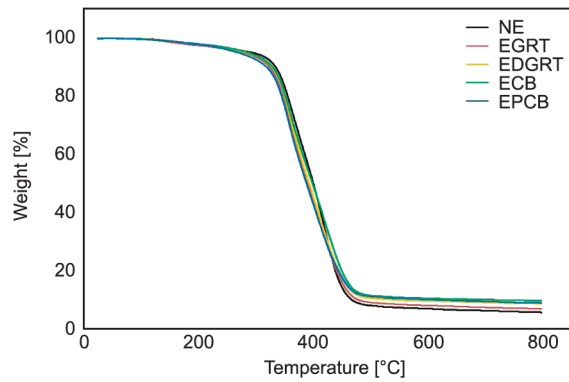


Figure 4. TGA curves of the neat epoxy and the composites. 800 °C increased with the addition of particles to the epoxy composites.

3.2. SEM analysis

The morphologies of the fractured surfaces of the epoxy matrix composites are given in Figure 5.

Table 2. TGA data of the neat epoxy and the composites.

	Weight loss temperature		Residues at 800 °C [%]
	5% [°C]	50% [°C]	
NE	294	399.8	5.65
EGTR	278	389.2	6.93
EDGTR	284	392.2	8.69
ECB	287	398.4	9.77
EPCB	268	387.7	8.90

Various mechanisms have been suggested in several studies on the toughening mechanisms of rubber-modified thermoset polymers, such as; shear deformations, cavitation caused by rubber debonding, and rubber particle bridging at the crack tip [33], crack deflection [11], crack blunting [8, 11]. In the GTR and DGTR particles modified epoxies, the main toughening mechanism was observed that the crack deflection and branching by the rubber particles, which

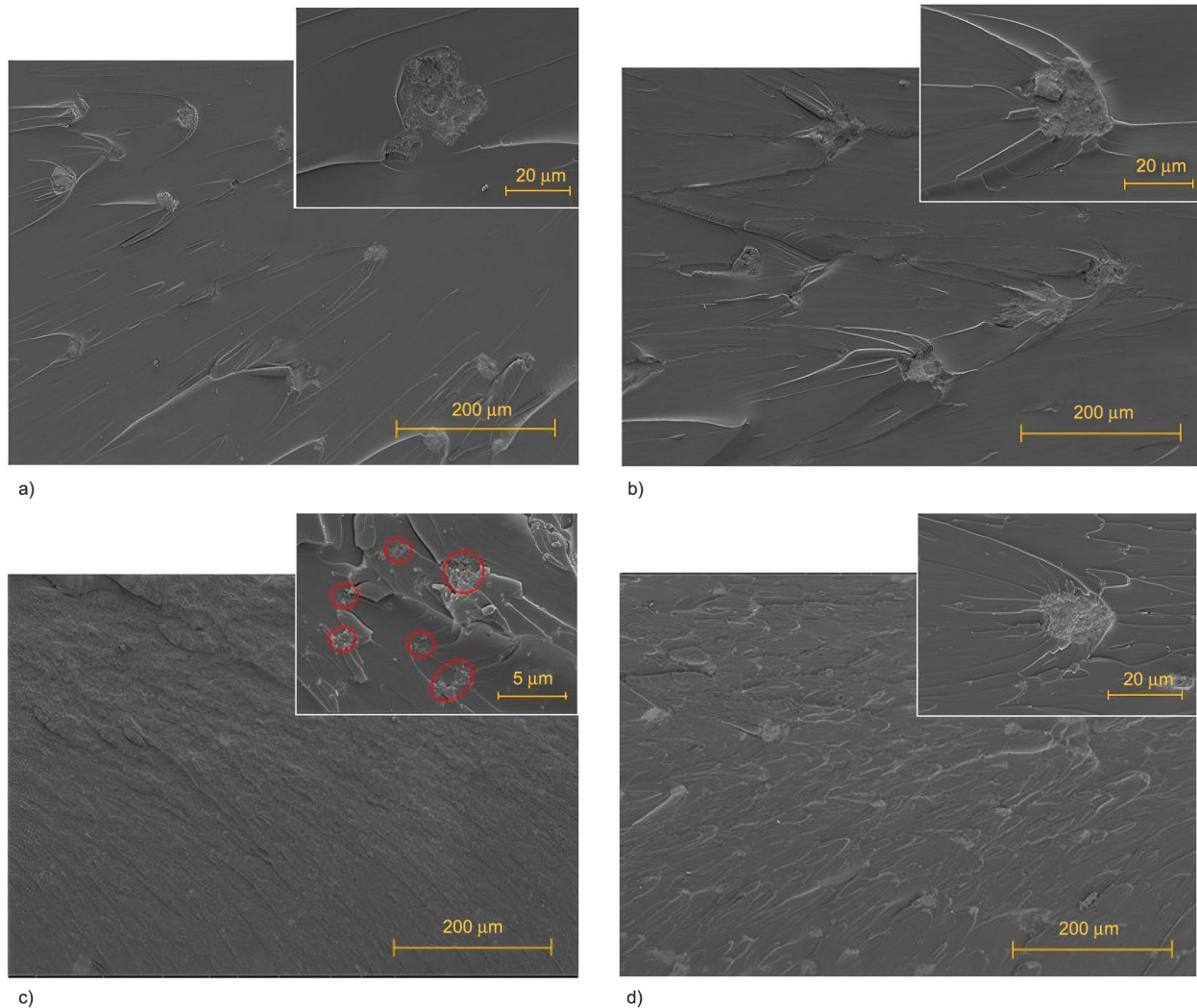


Figure 5. SEM micrographs of the fracture surface of the epoxy composites and the adhesion between epoxy matrix and particles; a) EGTR, b) EDGTR, c) ECB, and d) EPCB (Red circles indicate agglomerations) (Magnification; low:150×, high: 2000×).

require more energy for crack propagation, and the secondary mechanism was that shear deformation which is ascribed to the strength of the matrix-filler interface [8, 11]. Microstructures with river-like lines are characteristic of these mechanisms (Figure 5a and 5b). This characteristic feature is also visible on the fracture surface of the PCB added epoxy (Figure 5d). It has also been observed that the fracture surfaces have crack propagation mechanisms, such as crack branching and deflection, which require more energy for crack propagation. Although the particle size of the PCB is in the same range as the size of the GTR particles, the river-like lines formed on the fracture surface of the EPCB sample appear to be more intense (Figure 5d). The morphology of the fractured surfaces of the ECB sample is presented in Figure 5c. It can be seen that the ECB sample exhibited a different fracture surface from the other samples due to the particle size of the CB. As shown in Figure 5c, the fracture surfaces of the ECB sample exhibited rough surfaces with randomly distributed cracks, but shear deformation was limited due to nanoparticle agglomeration.

SEM analysis also shows that the dispersion of GTR, DGTR and PCB particles in the epoxy matrix is homogeneous (Figure 5). Particle agglomeration observed from the EPCB sample due to the particle size of the PCB is nanosized. In addition, the fracture surfaces of all composite samples were examined in detail with the SEM analyses to observe the interaction between the particles and the epoxy resin system, and it can be seen in Figure 5 that there is a strong adhesion at the interfaces.

3.3. Adhesion behaviour of composite coatings

The cross-cut test was used to determine the degree of adhesion of the coatings to the galvanised steel substrate. Adhesion is graded through the following criteria, according to the percent of the removed area after cross-cutting: 0B (>65% coating removal, low adhesion), 1B (35–65%), 2B (15–35%), 3B (5–15%),

4B (<5%), and 5B (0%, no coating removal, high adhesion). The adhesion test results presented in Figure 6 show that the coatings exhibit high adhesion (5B). It was found that the addition of GTR, DGTR, CB and PCB particles did not adversely affect the adhesion of the tested epoxy coatings.

3.4. Mechanical properties

The effect of particles on the hardness and elastic modulus of the epoxy matrix is shown in Table 3. It is seen that the particles added to the epoxy matrix produce two different results. While the hardness of NE was improved by about 8% for EGTR coated sample, the hardness was dropped by about 59, 58 and 60% for EDGTR, ECB and EPCB coated samples, respectively. The limited increase in hardness and modulus of composite coatings with the addition of GTR particles can have several reasons. The strong interfacial interaction between the epoxy matrix and the GTR particles, which caused a decrease in the molecular mobility of the polymer chains by the particles, caused an increase in the mechanical properties [5, 34]. In addition, Adesina *et al.* [28] suggest that the presence of a second phase at the interface between epoxy and GTR that favours resistance to plastic deformation leads to improvement in mechanical properties. In the same study, Adesina *et al.* [28] also suggested that the presence of different size pores on the surfaces of the GTR particles may contribute to the interaction with the epoxy resin molecules that penetrate and fill the pores, thus enabling improved blending between the epoxy resin and GTR reinforcement. It is well known that the mechanical properties of composites are affected by the physical and chemical properties of the reinforcement particles. The properties of all particles used in this study are given in the previous sections. In Figure 1, it can be seen that the surfaces of the DGTR particles are rougher than the surfaces of the GTR particles, furthermore, the surface area of the DGTR particle is about 17.5 times that of the GTR. The expected

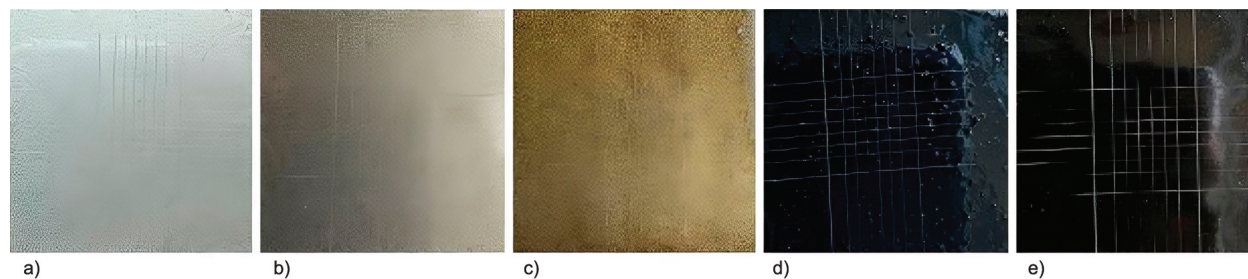


Figure 6. Images of coated samples after cross-cut test; a) NE, b) EGTR, c) EDGTR, d) ECB, and e) EPCB.

good interaction between DGTR particles and epoxy matrix was observed in SEM analyses (Figure 5). However, while this interaction is expected to cause an increase in the hardness and modulus of the composite, the results show the opposite. It is thought that this may be due to the structural changes that occurred during the devulcanisation of the GTR. Microwave treatment of GTR primarily caused crosslink (S–S) scission and partial main chain (C–C, C–S) degradation. In addition, other changes may have occurred due to the composition of the GTR, such as, increasing carbon black and residue content with the partial decomposition of NR chains (Table 1). These changes show that the elastomeric characters of GTR are not present in microwave devulcanised GTR and that DGTR acts as a different filler and affects the properties of epoxy composite similar to carbon black. Similar results have been presented in a limited number of studies, and it has been reported that the time and energy of the microwave process also affect the GTR properties, which in turn affects the interaction of DGTR with the epoxy matrix and the mechanical properties of the composite [29, 35, 36]. Table 3 shows that adding CB and PCB to the epoxy matrix reduces the hardness and modulus of the composites, similar to DGTR. The use of commercial carbon black used in this study in nano size is the most important difference from other particles added to the epoxy composite coating. It is generally known that nanoparticles easily agglomerate due to their large specific surface area and high surface energy [37, 38]. In this study, the agglomeration of CB added to the epoxy matrix is also clearly seen in the SEM analysis (Figure 5). The agglomeration of carbon black particles can cause poor energy dissipation under load, hence becoming the stress points of the polymer composites, thus, the mechanical properties of the composite are reduced [31, 39]. From the results, the incorporation of PCB into the epoxy matrix also reduced the stiffness and the modulus, which could be explained by poor stress transfer between filler and matrix [31]. The properties of the carbon

black obtained after the pyrolysis process are given in Table 1, and the surface morphology is also seen in Figure 2. Although a sufficient interaction between epoxy and PCB was observed in the SEM analysis (Figure 5), it is thought that high ash and carbonaceous deposits on the surface of CB and surface morphology are effective in reducing the hardness and modulus of the composite.

Microscratch test results of the epoxy composite coatings are given in Table 3. It was observed that the penetration depth increased in all composite coatings compared to the neat epoxy coating. However, it is seen that increasing the penetration depth of the CB added coating is very high compared to the others. The nanoscale of the CB added to the coating and its tendency to agglomerate affected the properties of the composite coating and caused the penetration depth to be obtained very differently from the other samples. In addition, the elastic recoveries after the scratch tests were increased in all composite coatings (Table 3). This result showed that the presence of particles facilitated the epoxy resin to deform in the elastic field, with most of the deformation occurring during the scratch and readily recovering after the release of the load.

3.5. Wear properties

The results obtained from the wear test are given in Figure 7. It can be seen that the NE and the ECB coated sample exhibited similar surface roughness. The surface roughness of NE was not significantly affected by the addition of CB. However, with the addition of GTR, DGTR and PCB particles, the surface roughnesses were remarkable reduced. The decrease in the surface roughnesses can be attributed to the particle properties, particle distribution and low amounts of particles.

The evolution of the coefficient of friction (COF) curves is presented in Figure 8, and the average COF is given in Figure 7. It is seen that the coefficient of friction values of all composite coatings are quite similar to each other. However, COF curves of the NE

Table 3. Indentation and scratch test (at an applied load of 5 N) results.

	Hardness [MPa]	Modulus [GPa]	Penetration depth [μm]	Residual depth [μm]	Elastic recovery [%]
NE	415.87±9.52	6.67±1.70	28.0	11.0	60.71
EGTR	449.93±15.81	9.50±1.92	36.4	12.5	65.66
EDGTR	172.65±4.85	3.24±0.08	35.0	11.8	66.29
ECB	174.44±2.28	3.32±0.06	84.2	10.0	88.12
EPCB	165.65±3.45	3.01±0.03	35.5	11.7	67.04

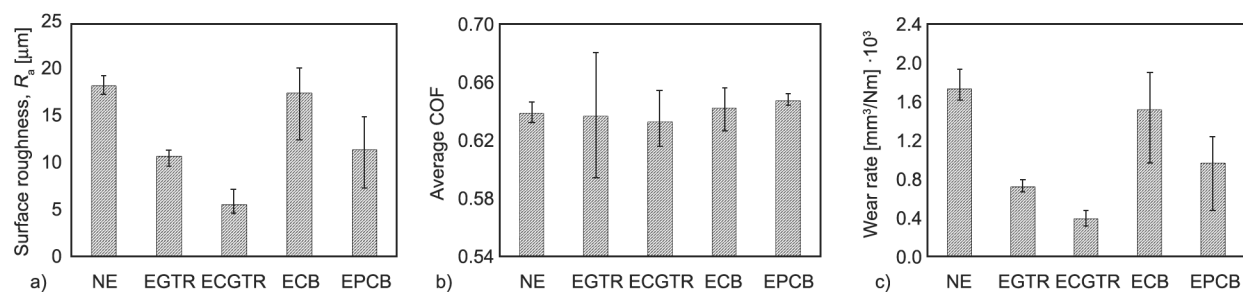


Figure 7. a) Surface roughness, b) average friction coefficient and c) specific wear rates of the coated samples.

and ECB and EPCB exhibited more fluctuations and instability over the total length, while with the GTR and DGTR loading, the fluctuations in the COF curve were significantly reduced, resulting in more stable and smoother COF curves throughout the total length. It is seen that the wear rate of composite coatings is reduced compared to the neat epoxy coating (Figure 7). The particle type and distribution in the composite, the particle and matrix adhesion, and the surface roughness of coatings affected the friction and wear properties of composites [40]. The filled with GTR and DGTR epoxy composite coatings show lower wear rates than those filled with CB and PCB particles. Specific wear rate values of the filled with GTR and DGTR epoxy composites are 59 and 77.7% lower than that of neat epoxy, respectively. The increase in the wear resistance of the EGTR coating is due to the increase in the hardness of the coating by the GTR particles. There have also been studies that attribute the reason for this increase in wear resistance to the rubbery properties of the particles [41]. However, in the EDGTR coating with the highest wear resistance, the wear behaviour was affected by the structural and surface properties of GTR that changed after devulcanisation, as well as the elastomeric character of GTR in part due to the scission of crosslinks after devulcanisation.

The highest wear rate among all composite coatings was observed in the nanosized CB added sample. The agglomerated particles potentially act as localised stress concentration points and, when the composites are introduced to wear, play an important role in material removal due to wear [42]. Coatings with PCB added did not behave like ECB due to the size of the PCB, but because it did not behave like rubber, the wear rate was higher than those reinforced with rubber but less than with epoxy. The high ash content of PCB may have contributed to the lower wear rate of EPCB coatings than ECB. The 3D profile images of the wear tracks after 300 m total sliding distance are

shown in Figure 8. It was measured that the width of the wear track was 1436 μm in the NE sample. With the addition of GTR, DGTR and PCB particles, the width of the wear track was decreased to 1067, 963 and 1303 μm , respectively. The wear track width of the ECB sample was obtained quite close to the NE sample and 1450 μm . The width of the wear track is related to the plastic deformation. Therefore, the increased plastic deformation resistance of the coating means that the wear rate will be lower [43]. In addition, the wear track of NE is around 73 μm deep, while that of other samples is about between 30 and 65 μm deep. As for the ECB and EPCB, the depth of the wear track for both samples was approximately 65 μm , which is about two times higher than that of samples EGTR and EDGTR. Compared to the NE coating, the maximum reduction in wear volume was obtained with 77.7% in the coating reinforced with DGTR, and the lowest decrease with 12.5% in the coating reinforced with CB.

SEM micrographs of the worn surfaces, which provide information about the wear mechanism during the sliding, are also given in Figure 8. For the neat epoxy coating, the presence of large amounts of cracks, cavities and deep ruptures indicates that the effective failure mechanisms are fatigue wear and abrasive wear [28, 43, 44]. This wear image also shows the brittle nature and insufficient toughness of the epoxy [28]. It has been observed that the CB added coatings also exhibit similar wear behaviour to the neat epoxy coating, it was clear that the effective stress transfer from the matrix to the CB network had not occurred due to the nanoparticle agglomeration. However, the ridgelines and pull-outs, which can be explained by fatigue or adhesion-slip phenomena during sliding, were observed in GTR and DGTR added samples. The wear mechanism has changed from brittle wear to sticky wear. It has been observed that there is a decrease in the ridgelines and peeling of the EDGTR sample compared to the

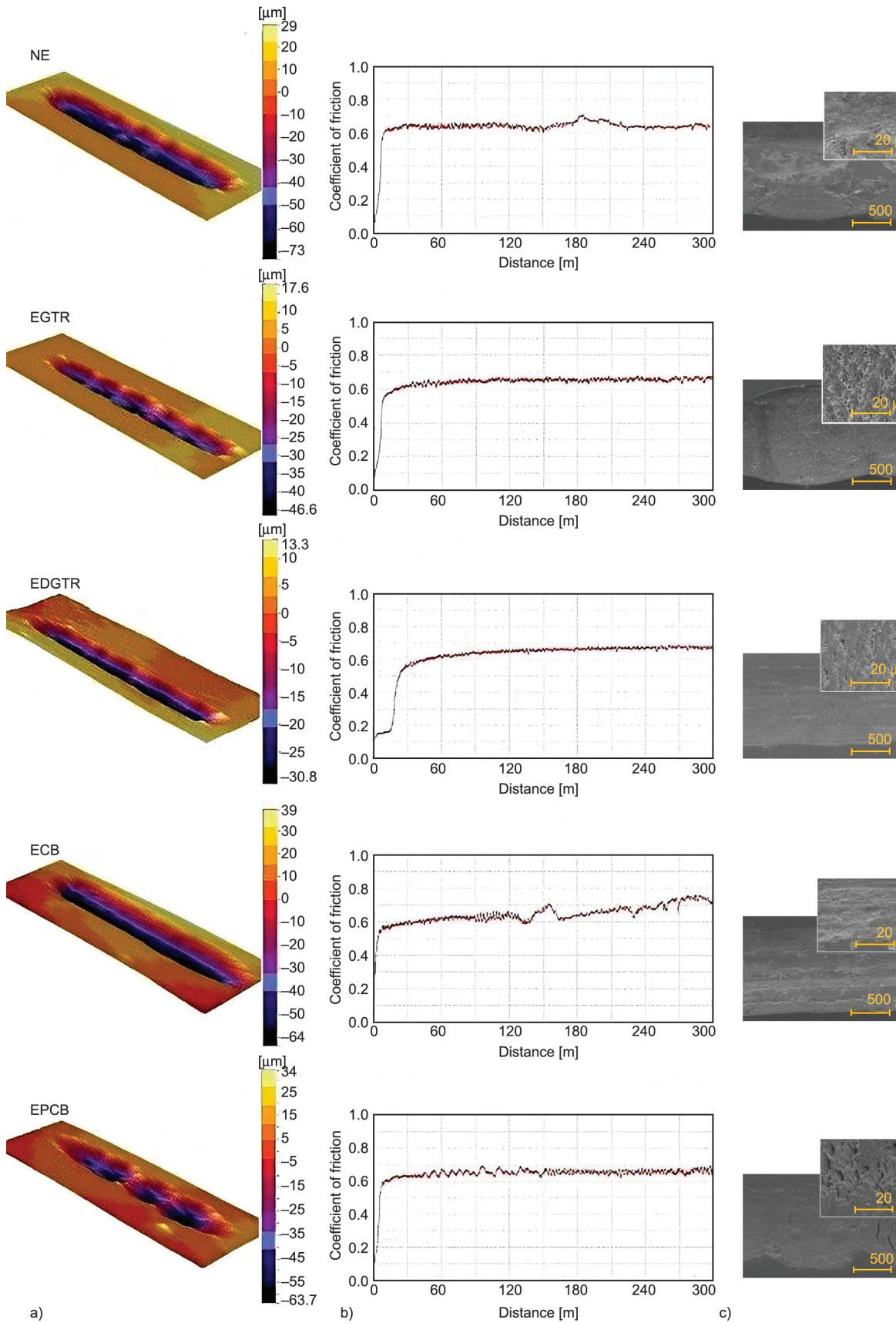


Figure 8. a) 3D profile images, b) frictional coefficient, and c) SEM images of worn surfaces of the coated samples (Magnification; low: 500 \times , high: 5000 \times , ECB high: 20 000 \times).

EGTR sample. This result also supports the increase in wear resistance. In the EPCB sample, a wear surface image was observed between the ECB sample and the EDGTR sample, and more damage was observed than in the EDGTR sample (Figure 8).

3.6. Corrosive properties

Salt spray test was carried out to examine the corrosive properties of the coatings, and the visual performances of the samples at the end of various periods are shown in Figure 9. No corrosion was observed in any of the samples exposed to salt spray for 10 days. Increasing the test time caused the formation and increase of white rust on the surface of the coatings. White rust is caused by corrosion of the galvanised layer between the steel substrate and the epoxy coating. The increasing white rust on the sample surface means that the oxidation rate of the sample is higher than the others. The addition of particles to the epoxy matrix causes a barrier effect by filling the free volumes and porosity of the coating, thereby reducing the oxidation rate of the zinc layer and increasing the cathodic protection time of the coating. As the exposure time to the corrosive environment increases, the protective effect of the zinc layer decreases and the barrier properties of composite coatings increase. The increasing white rust also caused the adhesion failure, delamination from the scratches and blister formation on the coatings (Figure 9).

Salt spray test results showed that the highest corrosion resistance was obtained in EPCB coating, although there was an improvement in the other composite coatings compared to the neat epoxy coating. During the salt spray test, no white rust was observed on the EPCB coating, but a small amount of blister formation was observed. Blistering degrees of the coated samples after 42 days were evaluated according to ASTM D-714-87/00 and were obtained as follows; 4F (NE), 2F (EGTR), 6F (EDGTR), 6M (ECB) and 8F (EPCB). The results can be attributed to the excellent barrier properties of PCB particles that do not let corrosive ions penetrate into the metal-coating interface and prevent blistering on the coating surface. Therefore, EPCB coating can provide excellent long-term protection against a harsh corrosive environment with a high concentration of chlorine ions. The increase in the barrier properties of PCB is due to its composition, as well as the more difficult migration of corrosive ions due to its more disordered structure (Figure 2). Studies have shown that

although the electrical conductivity of PCB decreases due to the lower carbon content, more disordered structure, and the high ash content (Table 1), various pyrolytic carbons produced at high pyrolysis temperature can exhibit fast electron transfer pathways through the carbon matrices [45, 46]. In addition, ash components and functional groups on the PCB can accelerate the formation of corrosion products that increase the barrier property of the coating [46].

4. Conclusions

In this study, various properties of the epoxy composite coatings reinforced with recycled waste tire products were investigated, and the following conclusions were reached:

- The hardness of the neat epoxy increased by approximately 8% when reinforced with GTR and decreased by approximately 59, 58 and 60% when reinforced with DGTR, CB, and PCB, respectively. A similar change was observed in the modulus of elasticity of the neat epoxy. The penetration depth increased in all composite coatings compared to the neat epoxy coating, with the greatest increase in the CB reinforced epoxy coating.
- The wear rate of all coatings with reinforced particles is reduced compared to the neat epoxy coating. Specific wear rates of the reinforced with GTR, DGTR, CB and PCB epoxy composites are 58.5, 77.7, 12.5 and 44.26% lower than that of neat epoxy, respectively.
- The corrosion resistance increased in all composite coatings compared to the neat epoxy coating, but test results showed that PCB reinforced epoxy coating showed the highest corrosion resistance.
- It has been seen in the SEM analyses that the distribution of all particles except CB in the epoxy matrix is homogeneous and that there is strong adhesion at the particle-matrix interfaces.
- The results obtained in this study offer an alternative way of improving the properties of epoxy composite coatings developed using waste tire recycling products, as well as suggesting new areas of use for the products obtained from the recycling of waste tires. This study revealed that all waste tire recycling products added to the epoxy matrix, especially devulcanised rubber, increase the wear resistance of the composite coating. In addition, it has been observed that pyrolytic carbon black contributes to the improvement of the corrosion resistance of the epoxy coating.

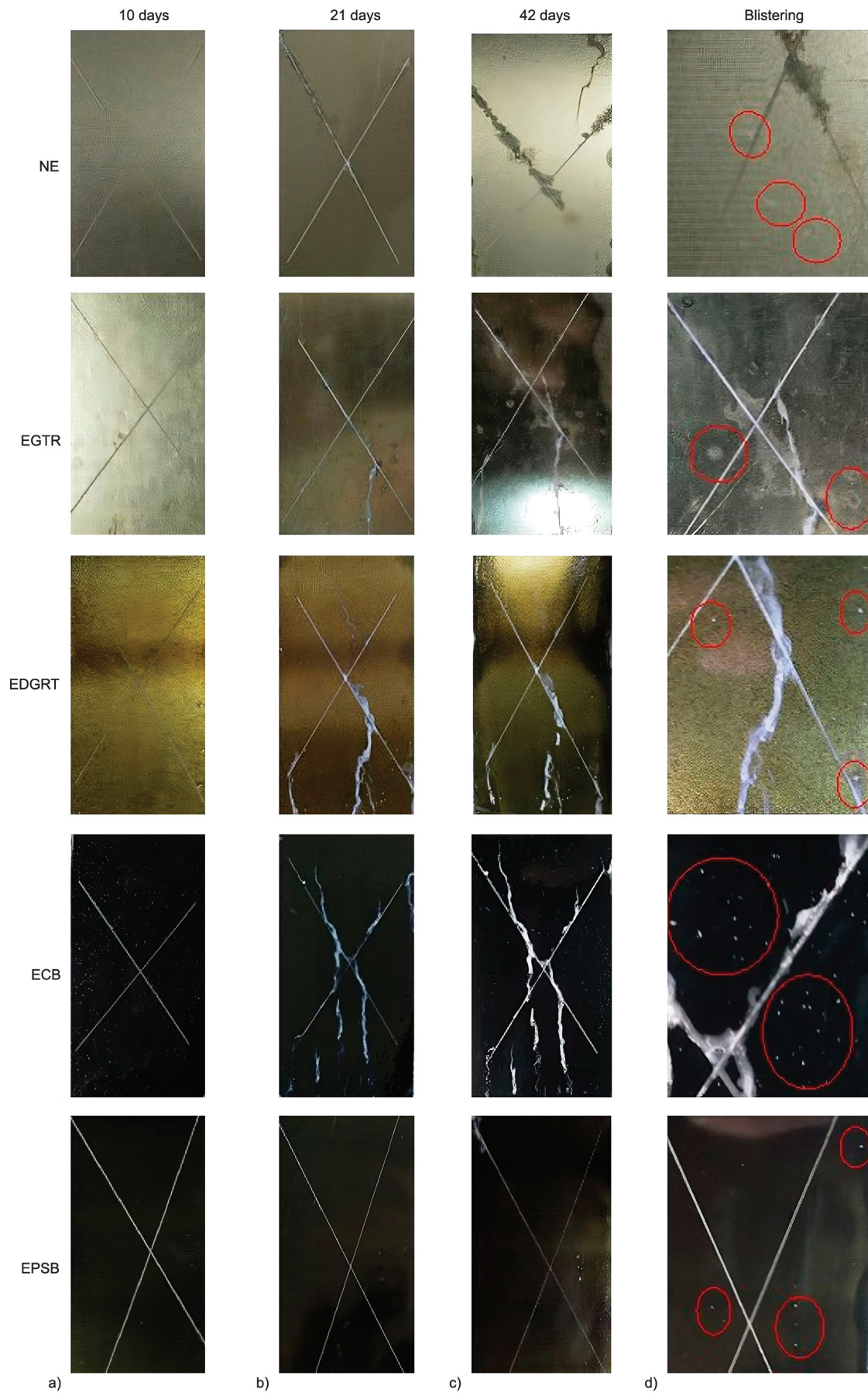


Figure 9. Photographic images of the neat epoxy and composite coatings after a) 10, b) 21, c) 42 days salt spray test, and d) blister formation after 42 days (Red circles indicate blisters).

- Nevertheless, it is not possible to simultaneously improve the various mechanical properties of recycled waste tire products reinforced epoxy matrix composite coatings. Because the results obtained are affected by the properties such as the size distribution, shape and agglomeration tendency of the particles, as well as the physical and chemical properties of the particles changed by the devulcanisation and pyrolysis processes. Further research is needed to reach a compromise between these mechanical properties before the application of these composite coatings becomes widespread.

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