

Research Article

Tailoring of Eco-Friendly Epoxies with Synergistic Adhesion Strength

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ABSTRACT

For sustainable development, eco-friendly epoxies, composed of recycled rubber micro-particles and core-shell rubber (CSR) nanoparticles, were processed to improve adhesion strength of an epoxy resin to structural steel substrates. To achieve this, the influence of mixing ratio of a recycled rubber micro-particles and CSR nanoparticles on the adhesion strength and adhesion fracture mechanisms of an epoxy were investigated in the present study. Synergistic adhesion strength was obtained for a certain combination of 7.5 parts per hundred resin (phr) CSR nanoparticles and 2.5 phr recycled rubber micro-particles. The remarkable increase in adhesion strength was attributable to “branching” of the crack-tip damage zone plus crack deflection to cause an adhesive to cohesive fracture transformation.

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1. Introduction

The global production of tires is increasing and, consequently, generated waste tires are ascending [1, 2]. Based on the global tire recycling market analysis by Goldstein [3], over 1.6 billion tires are annually produced and the number of waste tires generated to the environment is stated to be around 1 billion units per year. The number of waste tires is projected to increase to 1.2 billion tires per year in 2030 [4]. This waste

growth at the end of a tires' life is a serious hazard to the environment and the existing entities of the universe. Thus, tire waste management has become vital [4]. One of the promising strategies for tire waste management is to use the recycled rubber of scrap tires to toughen polymers, such as brittle epoxies.

Toughened epoxies containing different types of modifiers are widely used in diverse industrial applications [5-7]. Marouf et al. [8] provided a comprehensive review on the toughening effect of the

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common modifiers used in epoxies. Among modifiers, rubbers can be utilized as adhesion modifiers in many adhesives and coatings [9-11]. The rubbery phase can be added into epoxies via three main approaches, including reactive oligomer elastomers, pre-formed rubber particles and block copolymers [12].

Pre-formed rubber particles, like core-shell rubber (CSR) particles, are effective modifiers for epoxies with the advantage of well controlled volume fraction and particle size in comparison to reactive oligomer rubbers. CSR particles consist of a rubbery core and a thin layer of a glassy shell. The chemical structure of the rubbery core and the glassy shell can be varied independently when the aim is core-shell morphology. Acrylic or butadiene-based rubbers are usually used as the core material and the shell is made of glassy polymers such as poly(methyl methacrylate), PMMA. The glassy shell prevents rubber particles from sticking to each other, hence preserving their size and shape. Furthermore, the glassy shell can be tailored based on the chemistry of the matrix and the preferred interface between the CSR particles and the matrix [12]. In addition, CSR particles have negligible or no negative impact on the modulus of epoxies.

Recycled rubber of scrap tires have been also successfully incorporated into many epoxies as pre-formed rubber modifiers [13-16]. Influences of a second rubbery phase in the form of reactive oligomers [17, 18], CSR particles [19-23], recycled rubber particles [6, 16, 24, 25] and block copolymers [18] on mechanical properties of bulk epoxies and epoxy-based adhesives and coatings have been studied extensively.

Particle size and size distribution are among the effective parameters to control the toughening effect of either rubber modifiers or nanofillers in epoxy matrices [12, 26]. Chen and Jan [27] prepared bimodal distributed liquid rubber particles in an epoxy resin and studied the fracture behavior of the modified epoxies. They found a synergistic increase in fracture energy when bimodal size rubber particles were used instead of unimodal ones. However, Pearson and Yee [19] did not observe any significant improvement in fracture energy in the similar bimodal rubber particle modification in epoxy resin.

Furthermore, investigations on the application of bimodal micron-size recycled rubber particles and liquid rubber on fracture toughness of epoxies have been conducted by several researchers [25, 28, 29]. These studies found that the fracture toughness can be improved dramatically by a certain combination of rubber particles [25, 29] and the toughening mechanisms responsible for this phenomenon was revealed by Bagheri et al. [25].

Gerace et al. [30] reported an improved shear-lap strength when micron-size recycled rubber particles were added to a liquid elastomer modified epoxy formulation. They addressed this behavior in their bimodal size rubber modified epoxies to the modification of the modulus of the adhesive. In fact, the recycled rubber particles of scrap tires increased the flexibility of the brittle epoxy adhesives and, consequently, caused the higher overlap shear strength and thick film cohesive failure modes [30]. However, they did not investigate the adhesion fracture micro-mechanisms to be responsible for their observation.

In practice, many factors can affect the adhesion strength of an adhesive, including the intrinsic toughness of the adhesive, the ability of the adhesive to wet the substrate, the bond thickness and the adhesive bonding area [30, 31]. The adhesive joint contains three areas: the substrate, the interface between the substrate and adhesive and the adhesive. Joint failure can occur in any of the three areas. Adhesive fracture occurs at the interface area when the interfacial adhesion is less than that of the intrinsic strength of the adhesive or the substrate. This fracture is indicated by a clean substrate surface after separation. Cohesive fracture occurs within an adhesive when the intrinsic strength of the adhesive is, generally, the weakest point. This is indicated by a coating of adhesive on both substrates. The adhesion strength value depends on the amount of energy which it may be dissipated in:

- (i) Crack tip damage zone during adhesive or cohesive failure: In fact, the crack growth resistance in adhesive or cohesive failure is related to the plastic deformation zone size induced at the crack tip.
- (ii) The boundary layer de-adhesion between the

polymer and the substrate: The adhesive strength is related to the required energy to create fractured surfaces which is equal to the thermodynamic work of adhesion [32-34].

It is noteworthy to mention that this adhesion work is equal to strain energy release rate (G) during de-adhesion [35]. The strain energy release rate in plain strain condition (G_{IC}) can be correlated to the fracture toughness value (K_{IC}) and elastic modulus of the material (E), i. e. $G_{IC} = K_{IC}^2/E$. It can be concluded that, in general, the adhesion strength depends on the fracture toughness value and the modulus of the material as reported by Gerace et al. [30].

Though rubber-toughening of epoxies is a well-established field with magnificent achievements, the possible effect of simultaneous introducing of micron-size recycled rubber particles and CSR nanoparticles on the adhesion strength of epoxy adhesives/coatings has not been studied, to the best of the authors' knowledge. In addition, as mentioned previously, a synergistic effect of bimodal size rubber particles was reported at a certain ratio of recycled rubbers to reactive oligomer rubbers on the fracture toughness of the bulk DGEBA epoxy [25]. However, the effect of content ratio of bimodal size rubber particles has not been explored on the adhesion strength of an epoxy-based adhesive/coating. Considering the mentioned gaps in the literature and the need for developing sustainable materials, the current research aims to formulate an eco-friendly epoxy with high adhesion strength for sustainable development of adhesive and coating applications. Furthermore, the dominant toughening micro-mechanisms of the bimodal size rubber modified epoxies formulated, are elucidated.

2. Experimental

2.1. Materials

Table 1 lists the materials used in this research. The epoxy resin used, was a mixture of two liquid diglycidyls; ether bisphenol A (DGEBA) resins, the most commonly used epoxies, Araldite® GY 6010 and Araldite® GY 257; both from Jubail Chemical Industries (JANA). The reason to select DGEBA based epoxies was that these types of epoxies are commonly used resins for flooring, coating and adhesive applications. A ratio of 4:1 of the resins was used. Araldite® GY 6010 with epoxy equivalent weight (EEW) of 182-192 g/eq is a standard general purpose unmodified DGEBA epoxy with medium viscosity according to its data sheet while Araldite® GY 257 with EEW of 180-192 g/eq is a low viscosity epoxy. The main reason for using Araldite® GY 257 was to lower the viscosity of the end formulation and thus, improve the processability and wettability of the material. The curing agent used was an amine-based curative, Aradur® 43 from Vantico Inc. Aradur® 43 is a low viscosity cycloaliphatic polyamine hardener with the amine number of 260-280 mg KOH/g.

Two types of rubber modifiers were incorporated in this study. Ground scrap tire particles were used as coarse particles with the size of $\leq 200 \mu\text{m}$ from Dena Tire Co. Core-shell rubber particles comprised of a methacrylated butadiene-styrene (MBS) copolymer with a PMMA shell from Rohm & Haas with an average particle diameter of 80 nm (PARALOID™ BTA 702), were incorporated as pre-formed rubber nanoparticles [5].

Table 1. List of materials used in this study

Material	Supplier	EEW [†] (g/eq)	Viscosity [*] (mPa.S)	Amine number (mg KOH/g)	Average particle size
Araldite GY 6010	Jana	182-192	11,000-14,000	-	-
Araldite GY 257	Jana	180-192	500-700	-	-
Aradure 43	Vantico Inc.	-	200-400	260-280	-
Ground scrap tire	Dena Tire Co.	-	-	-	$\leq 200 \mu\text{m}$
PARALOID™ BTA 702	Rohm & Haas	-	-	-	$\approx 80 \text{ nm}$

[†]: Epoxy equivalent weight

^{*}: Viscosity at 25°C

St37 steel bars, from Mobarakeh Steel Co., were utilized as metal substrates to measure the adhesion strength of the epoxy blends processed. The surface contaminates of steel substrates were removed by applying a detergent followed by acetone degreasing prior to an application of the adhesive.

The processed formulations were summarized in Table 2. For unmodified samples, the neat epoxy resin and 60 per hundred resin (phr) curing agent were mixed for 20 minutes at room temperature. The resin was poured on the steel substrate to prepare T-peel test samples. Vacuum was applied to prevent bubble formation inside the resin during curing process. The adhesive-layer thickness was kept constant at 250 μm using copper wires as shim spacers. Before applying the adhesive layer on the steel substrate, the copper shims were glued to both sides of the steel substrate to control the thickness and uniformity of the adhesive layer in T-peel specimens. The epoxy resin was also cast into a Teflon coated aluminum mold to prepare characterization specimens. All samples were cured for 24 h at room temperature followed by 60 minutes at 100°C. It is important to minimize processing stresses and avoid thermal degradation of organic ingredients during the curing while, at the same time, attaining a complete curing process [10]. Thus, in the first step, the specimens were cured 24 h at room temperature to minimize processing stresses at the interface between the adhesive layer and the substrates and subsequently, the second step of curing was employed to ensure the curing process was complete and eliminate any possible differences in curing conditions affected from environmental conditions and or presence of rubber modifiers.

In the case of epoxy-rubber blends, in order to provide better mixing and prevent trapped bubble, the epoxy resin was pre-heated for 1 h at 80°C. The micron and nano-size rubber particles were mechanically mixed with the pre-heated epoxy resin in the given ratio (Table 2) for 30 minutes. As seen, the total composition of all samples containing nano and micro-particles were kept constant at 10 phr. The curing agent was then added in the given ratio to the epoxy-rubber mixture. Subsequently, the curing process occurred under vacuum conditions. The sample preparation was similar to the neat specimens.

2.2. T-Peel test

Adhesion strength of the epoxy resin to the structural steel substrates was measured using a T-peel test, according to ASTM D1876-95. A universal H10KS Hounsfield tensile frame with cross-head speed of 127 mm/min was used to determine the adhesion strength. Ten specimens were applied for the T-Peel test of each formulation.

2.3. Microscopy

Scanning electron microscopy (SEM): Fracture surface of some specimens were examined using a JEOL JXA-840 scanning electron microscopy (SEM) at an accelerating voltage of 20 kV. To avoid electron discharge of the specimens, fracture surfaces were coated with a thin layer of gold prior to microscopy.

Transmission optical microscopy (TOM): Double edge notched four-point bending test (DEN-4PB) was applied to investigate crack-tip damage zone micro-mechanisms. The DEN-4PB damage zone of the sub-

Table 2. Nomenclature terms of the rubber-toughened epoxy adhesives formulated in this study

Nomenclature	Composition		
	Epoxy resin (phr)	Recycled rubber micro-particles (phr)	Core-shell rubber nanoparticles (phr)
Neat epoxy	100	0	0
E10C	90	10	0
E2.5/7.5FC	90	2.5	7.5
E5/5FC	90	5	5
E7.5/2.5FC	90	7.5	2.5
E10F	90	0	10

E: Epoxy

critically propagated crack was cut along crack growth direction, but perpendicular to the fracture surface, using a diamond saw. After polishing down the TOM specimens to about 100 μm thickness, the dominant fracture toughness micro-mechanisms were explored using an Olympus EMP3 optical microscope under transmitted mode.

3. Results and Discussion

Fig. 1 illustrated the force-extension plots of different blends of epoxy resin obtained from T-peel tests. At first regime, the T-peel test curve showed an initial peak due to the energy consumption that created an initial sharp cohesive or adhesive crack. Then, a force drop occurred at the beginning of crack propagation. The crack propagation (second regime) carried out at almost constant force until the final fracture happened. In fact, the average adhesion strength was measured at this regime. As seen, most of the prepared blends showed a similar force level at the second regime. It meant that the adhesion strength was almost the same. However, the hybrid blend containing 7.5 phr nanoparticles and 2.5 phr recycled rubber micro-particles (E7.5/2.5FC) shows a dramatic increase in the adhesion strength. Fig. 1 also suggested that crack initiation occurred at almost relatively similar extensions in all formulations. This needs supplemental studies.

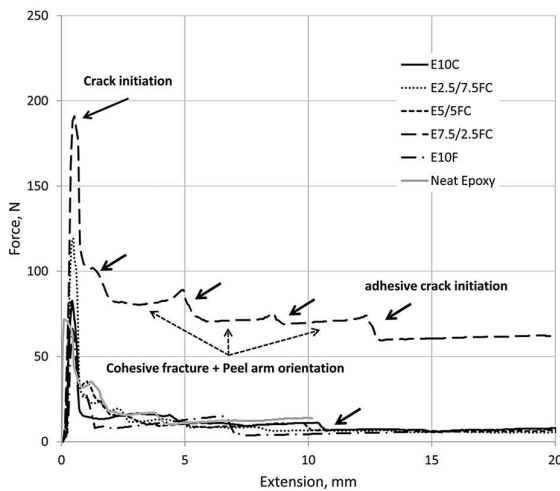


Fig. 1. Force-extension curves for different epoxy-rubber blends obtained from T-peel test.

The results of adhesion strength according to rubber composition are plotted in Fig. 2. Interestingly, the adhesion strength of this composition was higher than that of E10F (7.5 phr nanoparticles) and E10C (10 phr micro-particles) blends. Therefore, it can be concluded that a synergistic adhesion occurred when this certain ratio of rubber nanoparticles and recycled rubber micro-particles was incorporated into the epoxy resin.

It may be questioned if the presence of rubber particles can influence the curing condition of the epoxy system which leads to the improvement in adhesion energy. In general, introduction of rubber modifiers can change the curing condition of epoxy systems depending on the chemistry of the epoxy resin, curing agent, rubber modifier and its functional groups. As an example, a catalytic effect of a liquid rubber introduction on the curing process of a DGEBA-based epoxy has been reported by researchers [36] while another group of researchers claimed a decrease in the curing rate of an epoxy when rubber modifiers were introduced into the epoxy [37]. The end groups of the modifier led to the mentioned catalytic curing reaction [36]. Curing condition is an important factor given that it can affect mechanical properties of the end product due to the dependencies of the epoxy network intrinsic characteristics formed during curing plus the morphology of the rubbery phase forms in the epoxy

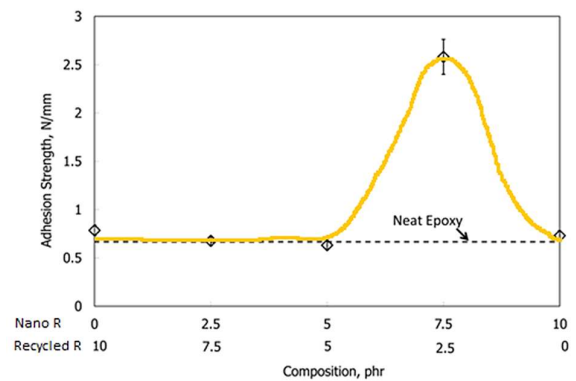


Fig. 2. Adhesion strength of epoxy resins to the steel substrate as a function of composition. The total rubber content was kept constant at 10 phr in all formulations. Note that the adhesion strength of the neat epoxy to the steel substrate is 0.667 N/mm. “Nano R” and “Recycled R” stand for core-shell rubber nanoparticles and recycled rubber micro-particles, respectively.

matrix containing either reactive oligomer rubbers or block copolymers [18]. In this work, we did not investigate whether the presence of rubber particles changes the curing kinetics of the epoxy system or not (this will be studied in our ongoing research). However, considering the probability of effect of rubber modifiers on the curing process, all of the samples containing rubber modifiers and the neat epoxy sample underwent a post cure cycle at 100°C for 1 h after the overnight curing at room temperature to avoid a likely incomplete curing process. The DSC analyses (not presented here) indicated that the curing processes of the epoxy systems with or without rubber modifiers were complete. It must be noted that, there was no concern of a morphology variation (size and size distribution of rubber particles) over the curing process since the pre-formed rubber modifiers with the certain sizes were used in this study.

According to Bagheri et al. [25], this synergistic behavior was also observed in fracture toughness of similar blend composition. In that study, the 7.5 phr/2.5 phr blend of fine and coarse rubber micro-particles showed a 16 % positive deviation from the rule of mixture in rubber toughened epoxies. In fact, it may be expected that the maximum fracture toughness for the epoxy containing 10 phr fine rubber micro-particles and minimum fracture toughness for the epoxy containing 10 phr coarse recycled rubber micro-particles. However, crack tip plastic zone enlargement and branching were the reason for the synergistic fracture toughness enhancement in the epoxy containing 7.5 phr fine rubber micro-particles and 2.5 phr coarse recycled rubber micro-particles. As previously mentioned, fracture toughness plays an important role in the adhesion strength of a resin. More energy consumption during crack propagation is expected when the fracture toughness of the material is higher and consequently, more adhesion strength can be expected. Therefore, it can be concluded that the synergistic effect seen in Fig. 2 was caused due to the very high fracture toughness of that formulation.

The effect of core-shell rubber nanoparticles on improvement of fracture toughness of epoxies is well-understood [12]. Generally, the rubbery cores in CSR

nanoparticles cavitate under tensile loading. The occurrence of cavitation inside the rubbery cores facilitates shear yielding; the main source of energy dissipation of the epoxy matrix around the crack tip. Thus, the fracture toughness increases by promoting localized plastic deformation of the epoxy matrix at the vicinity of the crack tip. The role of glassy shell in nanoparticles is to control size and dispersion of particles in the matrix. Rubber cores in the absence of glassy shells can stick together and form undesired particles in size and shape. The shell also helps control surface chemistry of the particles to obtain a favorable interface between the nanoparticles and the matrix. Moreover, the high stress field of recycled rubber micro-particles interact with the crack tip stress field causing comfort of cavitation of CSR nanoparticles and consequently, plastic deformation of the matrix around the recycled rubber micro-particles. Therefore, plastic deformation stretches out from the vicinity of the crack tip towards the recycled micro-particles. This enlargement of the plastic deformation zone causes remarkable increase in the fracture toughness [25].

Fig. 3 illustrated the schematic crack tip damage zones of the epoxy blends obtained from T-peel test. In the case of E10F blend (Fig. 3(a)), the fracture process was adhesive. The crack initiation occurred at the interface of the epoxy and steel substrate and crack growth continued on the same surface until the final fracture. It is concluded that rubber particle cavitation and, subsequently, shear yielding of the matrix is the major toughening mechanisms in rubber incorporated epoxies [12, 25, 38]. As seen in Fig. 3(a), the rubber particle cavitation and shear yielding caused an affected zone at the vicinity of adhesive crack tip with dimensions that took up half of a bulk crack tip damage zone size. Fig. 3(a-1) showed the TOM image of DEN-4PB damage zone for similar composition studied by Bagheri et al. [25]. The cavitation of rubber particle was caused by the hydrostatic stress field at the crack tip. The induced plastic deformation dissipated energy during adhesive fracture and a 9.4% improvement in adhesion strength can be gained in comparison to the neat epoxy resin (Fig. 2). Thus, one may

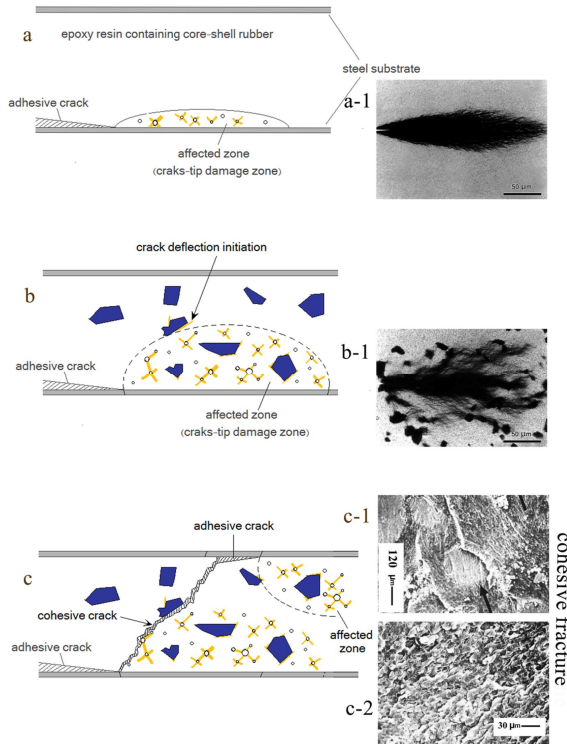


Fig. 3. Schematic representation of crack growth in T-peel test for: (a) epoxy containing 10 phr rubber nanoparticles, (b) epoxy containing 10 phr recycled rubber micro-particles, and (c) epoxy containing 7.5 phr rubber nanoparticles/2.5 phr recycled rubber micro-particles. Microscopy micrographs are reproduced from [25] by permission of John Wiley and Sons.

expect lower adhesion strength for the E10C sample because of lower fracture toughness value in comparison to the E10F sample. Interestingly, the adhesion strength for E10C was 17.8% higher than that of the neat epoxy. It was noteworthy that, while the difference between the fracture toughness value of E10F and E7.5/2.5FC samples was about 16% (positive deviation from rule of mixtures), the amount of deviation when the adhesion strength was 277%. Therefore, it can be concluded that the fracture toughness increment cannot be the only factor for this synergistic phenomenon.

In the case of E10C, no evidence of shear deformation at crack tip was observed. Instead, stress concentration on large rubber particles and subsequently micro-cracking and crack path deflection was the dominant fracture toughness mechanisms [25]. During the T-peel test the micro-cracking and crack path deflection causes adhesive to cohesive fracture transformation. However, the crack jump from initial

surface to the opposite surface through an adhesive-cohesive-adhesive fracture transformation can be expectable. This transformation introduced a force increment and a subsequent force level drop at the second regime of the T-peel test (indicated by arrows in Fig. 1). Therefore, the higher adhesion strength of E10C sample in comparison to E10F can be explained through stress concentration effect of the large scrap tire particles and the crack deflection and change in the fracture surface. Consequently, following effective energy dissipation the following mechanisms are activated:

- (i) Cohesive crack growth through the epoxy resin between two steel strips with a full crack tip damage zone size (twice the adhesive fracture affected zone).
- (ii) Change of the peel arm orientation that causes some strain in the steel strip due to the fracture surface variation (crack jump) [39].

In addition, the incorporation of recycled rubber micro-particles may cause the reduction in curing shrinkage of epoxy resin which introduces lower remained internal strain and improvement in adhesion strength. Overall, the internal strain is introduced close to the interfacial layer caused by resin shrinkage during the curing process.

Obviously, in the same conditions, the cohesive fracture dissipates twice the energy in comparison to adhesive fracture. In fact, the fracture toughness value plays more important role in the cohesive fracture than that of the adhesive one. However, since the fracture toughness value of E10C was much lower than that of E10F the cohesive fracture was not significant in terms of energy consuming mechanisms. Thus, as can be seen in Fig. 1, one can accept the comparable adhesive strength between E10F and E10C samples.

Synergistic adhesion strength for the E7.5/2.5FC formulation can be explained via activation of the following mechanisms. Enlargement of the crack tip damage zone (affected zone) caused by plastic zone branching and stretching was observed by Bagheri et al. [25] (Fig. 3(b)). It is obvious that the larger plastic zone the more energy dissipation is caused during adhesive fracture. According to Bagheri et al. work [25] shown in

Fig. 3(b-1), similar to E10C, the large rubber particles from the scrap tire can cause micro-cracking and crack path deflection. The crack deflection can induce cohesive fracture through epoxy resin between two steel strips (Fig. 3(c)). In contrast to E10C, E7.5/2.5FC showed high fracture toughness value through the cohesive fracture and, consequently, caused significant energy dissipation during the T-peel test. Therefore, the intrinsic fracture toughness of the adhesive introduced more effective influence on the adhesion strength value.

Fig. 3(c-1) showed the SEM micrograph of the fracture surface for E7.5/2.5FC. As seen, the large rubber particle introduces the micro-cracking and, subsequently, cohesive fracture (indicated by arrow). The higher magnification of the cohesive fracture surface is also shown in Fig. 3(c-2). As illustrated, the rubber nanoparticles induced an intense plastic deformation caused by rubber particle cavitation and shear yielding of the epoxy matrix.

Similar to E10C sample, the crack surface jump was also observed in E7.5/2.5FC sample. The crack jump caused a consecutive change in the peel arm orientation during T-peel test and some plastic deformation in the steel strips. This phenomenon can induce further force increment between two force drops (at the second regime) in addition to force increment due to the cohesive fracture.

Another noteworthy point (shown in Fig. 1) was the higher force required for crack initiation of the E7.5/2.5FC sample in comparison to the other compositions. This specific property was not considered in the adhesion strength measurement. However, it is a considerable property for adhesives. The high crack initiation force can be explained by the high fracture toughness for this certain composition.

4. Conclusion

The influence of mixing ratio of recycled rubber micro-modifiers and core-shell rubber (CSR) nanoparticles on the adhesion strength of an epoxy was investigated in this study. Based on the obtained results, the following conclusions can be drawn:

- Synergistic adhesion strength of the eco-friendly epoxy blend to the steel substrate was observed at a certain composition containing 7.5 phr nano-size and 2.5 phr micron-size rubber particles.
- The significant increase in adhesion strength can be attributed to the high fracture toughness of the above-mentioned blend mixture and also the change of adhesion fracture mechanisms from adhesive fracture to the combination of cohesive and adhesive fracture which can make a serrated fracture surface on steel substrate.

Conflict of Interests

The authors declare no conflict of interest.

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