Final Report

Toughening Mechanisms in Hybrid Nanocomposites of Epoxy Resin Modified with Rubber and Silica Nanoparticles

By Dr. Peerapan Dittanet

July/2016

Contract No. TRG5780252

Final Report

Toughening Mechanisms in Hybrid Nanocomposites of Epoxy Resin Modified with Rubber and Silica Nanoparticles

Researcher	Institute
1) Dr.Peerapan Dittanet	Faculty of Engineering, Kasetsart University
2) Assoc. Prof. Dr.Paisan Kongkachuichay	Faculty of Engineering, Kasetsart University

This project granted by the Thailand Research Fund

Abstract

Toughness of epoxy resins was significantly enhanced with two types of reinforcing agents, silica nanoparticles and epoxidized natural rubber. Diglycidyl ether of bisphenol A (DGEBA) cured cycloaliphatic polyamine was used as epoxy system. Silica nanoparticles (SN) with average particle size of 20 nm in diameter and epoxidized natural rubber (ENR) containing 50% mole of epoxide group were used as reinforcing agents. Thermal and mechanical properties of hybrid SN-ENR epoxy nanocomposites such as glass transition temperature (T_g), Young's modulus and fracture toughness were investigated. For a single filler system, the addition of ENR resulted in reduction of T_g and modulus of epoxy resins, whereas the addition of SN resulted in slightly increased values of T_g and significantly improved modulus. However, for the hybrid ENR-SN nanocomposite systems, the enhancement in both T_g and the Young's modulus were observed. Interestingly, the addition of a few weight percent SN to an ENR toughened epoxy can lead to more than doubling of the K_{IC} value. Through visual evidence via SEM, particle cavitation of rubber particles and particle debonding of silica nanoparticles were attributed to be responsible for the toughness improvements for epoxy. A possible explanation is that the presence of SN may increase ductility of the epoxy matrix around the ENR particles and facilitate the particle cavitation, which simply increase the toughness of epoxy resin.

วัตถุประสงค์ของการวิจัยเพื่อการศึกษากลไกต้านทานการแตกหักและสมบัติเชิงกล/เชิงความร้อนของวัสดุผสมอีพ็อกซีเรซินยางธรรมชาติและนาโนซิลิกา ในงานวิจัยนี้ทำการปรับปรุงและศึกษาสมบัติของอีพ็อกซีเรซินด้วยการเติมวัสดุธรรมชาติสองชนิด ได้แก่ ยางธรรมชาติอีพ็อกซีไดซ์ และนาโนซิลิกาที่มีขนาดเส้นผ่าศูนย์กลาง 20 nm จากการทดลองพบว่าการเติมวัสดุผสมร่วมทั้งสองชนิดลงไปในอีพ็อกซีเพื่อให้ได้ไฮบริดคอมโพสิทของอีพ็อกซีเรซินยางและนาโนซิลิกนั้น ส่งผลกระทบต่อ Tg เล็กน้อย แต่พบว่าค่ามอดุลัสของและค่าความต้านทานการแตกหักมีค่าเพิ่มขึ้นอย่างเห็นได้ชัด กลไกการเสริมแรงของวัสดุผสมร่วมทั้งสองเกิดจากการกระจายพลังงานแบบ particle cavitation ของวัสดุผสม กล่าวคือเมื่อวัสดุได้รับแรงกระทำจากภายนอกแรงดังกล่าวจะส่งไปยังวัสดุเสริมแรงและจะทำการต้านแรงนั้นโดยเกิดการฉีกขาดภายในและเกิดการกระจายพลังงานออกไป ทำให้อีพ็อกซีรับแรงกระทำจากภายนอกได้มากขึ้น ซึ่งกลไกดังกล่าวสามารถตรวจสอบได้ด้วยกล้องจุลทรรศน์แบบส่องกราด องค์ความรู้ที่ได้สามารถนำไปพัฒนาดวัสดุและการออกแบบผลิตภัณฑ์ที่ต้องการความแข็งแรงทนทานในการใช้งานได้

Keywords : epoxy, silica nanoparticles, natural rubber, toughening mechanisms

Project Code : TRG5780252

Project Title :Toughening Mechanisms in Hybrid Nanocomposites of Epoxy Resin Modified with Rubber and Silica Nanoparticles

Investigator :

1) Dr.Peerapan Dittanet	Faculty of Engineering, Kasetsart University
2) Assoc. Prof. Dr.Paisan Kongkachuichay	Faculty of Engineering, Kasetsart University

E-mail Address : fengppd@ku.ac.th

Project Period : July 15th, 2014 to July 15th, 2016

Executive summary

Epoxy resins are commonly toughened by rubbers, core-shell particles, thermoplastics, and silica particles; however, a new hybrid material could be a novel approach not only for toughening performance but also for improving mechanical properties. Traditionally, adding rubber particles is the most successful method to toughen epoxies but there is often a trade off with incorporating this modifier. Unlike soft rubber particles, rigid fillers have been found to be effective toughening agents for thermosetting resins without the loss of modulus and change in T_g. Although the rigid fillers do not increase the toughness as dramatically as rubber particles, the modulus and hardness are much higher than rubber-modified counterparts. Therefore, a new strategy is to take advantage of different toughening mechanisms from the attributes of soft rubber particles and rigid fillers. Thus, this work focuses on the addition of silica nanoparticles dispersed with epoxidized rubber particles for toughening epoxy. Epoxy matrix consisted of standard diglycidyl ether of bisphenol A resin (DGEBA). The silica nanoparticles with the particle size of approximately 20 nm were used, and epoxidized natural rubber was used as a second filler in the epoxy matrix. For single component systems, it was revealed that the addition of ENR resulted in the reduction in the T_g and modulus of epoxy resins, whereas the addition of SN resulted in slightly increased values of T_g and significant improvement in the modulus. However, the enhancement in both T_g and the Young's modulus for hybrid ENR-SN nanocomposites were observed. Interestingly, the addition of a few weight percent SN to an ENR toughened epoxy can lead to a doubling of the K_{IC} value. The improvements in toughness were visually evidenced using scanning electron microscopy. Particle cavitation of rubber particles and particle debonding of silica nanoparticles were observed and are attributed to be responsible for the toughness improvements for epoxy. The presence of SN particles may increase ductility of the epoxy matrix around the ENR particles and facilitate the particle cavitation, which simply increase the fraction of epoxy matrix that has plastically deformed.

Objectives

1. Elucidate the role of silica nanoparticles in rubber toughened epoxy resins
2. Study the role of silica nanoparticles in toughening hybrid epoxy-silica-rubber nanocomposites

Introduction

Epoxy resins are thermosetting polymers used extensively in structural and specialty composite applications such as adhesives, coating, encapsulates, casting materials, potting compound and binders [1-3]. Epoxy resins have good properties such as modulus and tensile strength, excellent chemical and solvent resistance, and dimensional and thermal stability [4]. When epoxy resins are cured, the resins are generally brittle due to a cross-linked structure [1, 3]. Therefore, modified epoxy systems through addition of different materials and approach are needed to overcome the shortcomings. One such modification of epoxy is to add toughening agents such as soft rubber particles, rigid inorganic fillers and semi-rigid organic fillers [4-15]. Soft rubbery particles are often found to be the most successful approach to toughen epoxies, however, the main drawback of using such modifiers is the reduction in modulus and glass transition temperature (T_g). Unlike rubber particles, rigid fillers, such as silica particles, have been found to be effective toughening agents for thermosetting resins without the loss of modulus and change in T_g. Although the rigid fillers do not increase the toughness as dramatically as rubber particles, the modulus and hardness are much higher than rubber-modified counterparts. Therefore, a strategy was developed to further enhance the fracture toughness of epoxies by taking advantage of different toughening mechanisms from the attributes of soft particles and rigid fillers. For example, hybrid composites consist of soft rubber and silica particles.

Silica nanoparticles (SN) have been commercially used on a large-scale for applications ranging from automobile tires to optical fibers and catalyst supports [16]. Silica particles can effectively improve the physical properties of polymeric materials such as hardness, toughness, heat resistance, wear resistance, and optical properties [17]. When inorganic particles are used in toughening epoxy resins, such as silica particles, a two-phase microstructure of randomly dispersed silica particles in a continuous epoxy matrix is obtained [18]. Various mechanisms have been proposed to explain these enhanced properties. Particle debonding is an important process that enables plastic void growth to occur in the polymer matrix. The presence of silica nanoparticles causes the stress to concentrate in the region between the particles and the matrix, resulting in the debonded particles at the particle-matrix interface [19]. This process largely depends on the degree of interfacial adhesion that is attained at the particle-matrix interface. Although the growth of voids or debonding in nanoparticles may dissipate a small amount of energy, this mechanism more importantly enables plastic void growth in the matrix to occur, which results in more dissipated energy and increases fracture resistance. For shear banding mechanism, stress concentration in the matrix results from the presence of the particles. The characteristics of shear banding induced by silica nanoparticles are similar to those observed in rubber particles. Particle debonding and void growth can give rise to the localized shear banding where debonding at the particle-matrix interface can greatly reduce the degree of triaxial stresses acting on the polymer matrix next to particles. This reduction of stress enables the further growth of shear bands. Shear yielding originates from the point of maximum stress concentration, where for inorganic particles, it is at the pole of the particles [9, 12, 20-25]

Epoxidized natural rubber (ENR) is an industrially established rubber and a chemically modified form of the cis-1,4-polyisoprene whereby some of the unsaturated unit on the molecular chain are converted into epoxide groups, which are randomly distributed along the polymer chain [26, 27]. The incorporation of ENR containing 50% of epoxide group (ENR-50) into the rubber blends has improved processability, stiffness, and resilience, as well as showed excellent oil resistance, reduced air permeability, and good damping and wet grip performance [28, 29]. ENR is also recognized as a compatibilizer for incompatible blends as well as a processing aid. In natural rubber-toughened epoxy resins, different performance can be expected from the characteristics of rubber particles (size, shape, and morphology) and the rubber-epoxy interactions, such as compatibility between the rubber and the epoxy and dispersion of rubber particles in the epoxy matrix [30]. It is generally accepted that the rubber particle cavitation induced matrix dilation mechanisms and plastic void growth of the matrix have been found as the major toughening mechanisms in rubber toughened epoxies.

In hybrid epoxy-SN-ENR composites, there is currently no exclusive interpretation of toughening mechanisms due to the complicated compositions and the interactions between various toughening mechanisms. Ideally, the addition of silica particles can toughen the epoxy and promote the rubber particle cavitation and shear band concurrently, resulting in considerable improvement in toughness. For example, Liang and Pearson studied mechanisms of toughening in hybrid epoxy-silica-rubber nanocomposites using carboxyl terminated butadiene acrylonitrile (CTBN), a synthetic rubber, as rubber particles and SN particles (20 nm and 80 nm) [5]. It was observed that the toughening effect of adding SN was significant to the fracture toughness of hybrid composites. The increase in fracture toughness with SN addition to CTBN-modified epoxies appeared to be an additive effect, and the toughening mechanisms in epoxy-rubber blends were found to be rubber particle cavitation that induced plastic matrix deformation. The silica nanoparticle escalates the deformation of plastic in the process zone in polymer matrix that enlarges the zone size in front of the crack tip. The authors proposed that this enhancement involved an increase in shear band density between rubber particles in the plastic zone. Sprenger et al. studied carbon fiber-reinforced composites using an epoxy resin matrix modified with reactive liquid synthesis rubber and SN and reported an increase in toughness but the loss in modulus and T_g [31-32]. It was found that the hybrid bulk resin with the highest addition level of SN exhibits the highest toughness and modulus. The agglomeration of modifying agents was observed and was caused by the presence of the reactive liquid rubber but no toughening mechanism of epoxy-rubber-SN composites were reported.

Based on the literature reviews, SN have been investigated as a toughening agent to rubber toughened epoxies with limited material space, and there is more to explore. Rubber particles mostly are based on synthetic rubbers used for toughened epoxies. To date, natural rubber toughened epoxies have not been reported which provide an opportunity for further development. This research includes the use of fracture mechanics to quantify the fracture toughness and elucidate the toughening mechanisms. The influence of the rubber modifier, silica nanoparticles, filler content and toughening mechanisms will be evaluated. This work will provide the general concepts of blending silica nanoparticles in rubber-toughened epoxies.

Literature reviews on toughening mechanisms in hybrid systems

The fracture toughening mechanisms in hybrid composites are highly complex due to the convoluted interactions between different material composites, effects of particle size and density of particles, and others, therefore, the toughening factors are not well understood. As such, there are many theories and model proposals aimed to deconvolute the various factors for toughened epoxy resins. In order to further understand the fracture behavior of hybrid nanocomposites, a brief review of the toughening mechanisms in modified and/or filled epoxies is given below. The current understanding of the toughening mechanisms for epoxy-silica composites will be first discussed, followed by epoxy-rubber composite materials, and finally, the hybrid epoxy-silica-rubber composites.

Toughening mechanisms in epoxy-silica composites

When inorganic particles, such as silica particles, are added to epoxy resins, a two-phase microstructure of randomly dispersed silica particles in a continuous epoxy matrix is obtained. Both physical and mechanical properties of the corresponding epoxy matrix can be improved due to the inherent properties of the silica particles. Various mechanisms have been proposed to explain these enhanced properties. These mechanisms include crack pinning/bowing, crack deflection, and microcracking [9]. For the crack pinning concept, the inorganic particles act as pinning points that stop crack propagation. Hence, the increased toughness can be expected by this mechanism. For the crack deflection toughening proposed, when the crack front approaches the particles, it is tilted and twisted out of its original plane. This action results in an increased fracture surface roughness due to non-planar cracks which consequently results in an increase in fracture toughness.

The size of the particles can have a significant impact on the overall toughness. According to the assumptions of those toughening mechanisms, the ability to stop the crack by pinning/bowing and crack deflection can only be effective if the particles are larger than the crack opening. Therefore, for particles with smaller sizes than the crack opening, it has been observed that these toughening mechanisms were ineffective. Recent work with very small particles have been shown to exhibit enhanced fracture toughening, however, the proposed mechanisms aforementioned cannot completely describe the behavior.

At present, there are many studies using nanometer sized fillers for epoxies filled inorganic particles, but only a few toughening mechanisms have been proposed for the toughening behavior . For instance, Johnsen *et al.* [25] observed nanoparticle debonding and subsequent void growth on fracture surfaces of epoxy-silica nanocomposites and suggested that plastic void growth was the major toughening mechanisms for epoxy/silica nanocomposites. Dittanet *et al.* [7] observed a thin dilation zone created by stresses concentrated on the surrounding areas of the silica nanoparticles which is formed by differences in Young’s modulus and Poisson’s ratio between epoxy and silica. However, matrix shear yielding was not observed. Liang and Pearson [20] argued that the plastic void growth is not the only mechanism for toughening by rigid nanoparticles in epoxy matrix. It was observed shear yielding near the crack tip region for epoxies filled with silica nanoparticles. Moreover, the increased fracture toughness was found to be dependent on the plastic zone size near the crack tip region and followed the Irwin formalized plastic zone model. The matrix shear yielding has been taken into consideration in calculating the dissipated energy responsible for the increased toughness in silica nanoparticle filled epoxy. However, an overestimation between the prediction and experiment was observed, and several adjustable parameters were used. Dittanet and Pearson [9] later modified the plastic void growth model from Johnsen’s study [25] and included the contribution energy from both shear banding and plastic void growth. It was experimentally observed that only small fraction of nanoparticles has ability to debond and initiate plastic void growth. By taking this into consideration, a reasonable agreement was observed. However, the model cannot quantify which toughening mechanism dominates in nanosilica filled epoxy resin. More recent work from Dittanet and Pearson [7] suggested that the shear banding mechanism dominates the toughening mechanisms in epoxy/silica nanocomposite system. By increasing the number of debonded nanoparticles, it was showed that the fracture toughness has been enhanced but not the size of the plastic zone. This result suggests that there might be additional mechanisms.

In conclusion, the toughening mechanisms that are considered to be responsible for increased toughness in silica nanoparticle modified epoxies are the debonding of silica nanoparticles followed by void growth and induced shear yielding of the matrix. Figure 1 shows a schematic illustrating the modes of deformation in silica nanoparticle-toughened polymers where the process usually exists ahead of the crack tip inside the plastic zone. This plastic deformation response at the onset of non-linearity in the stress-strain curve (strain-softening region).

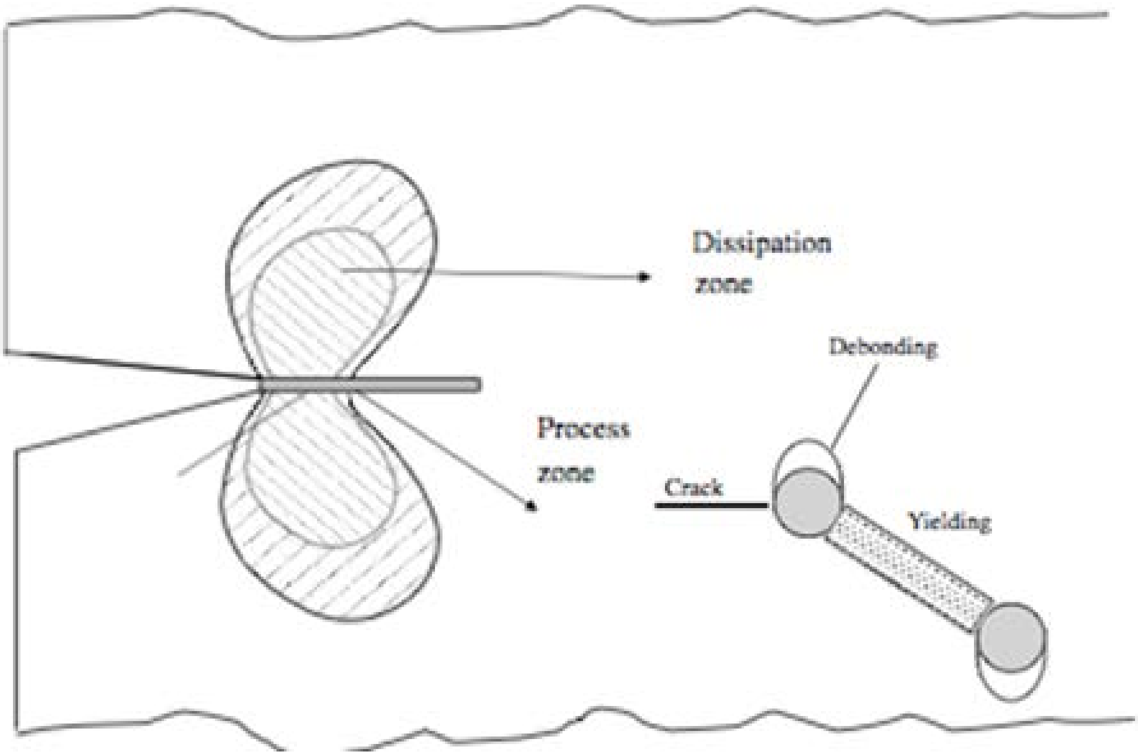


Figure 1. Particle debonding with subsequent plastic void growth and matrix shear yielding within the process zone. (Redrawn from Lauke [23]).

Particle debonding with subsequent void growth is an important process that enables plastic void growth to occur in the polymer matrix. The presence of silica nanoparticles causes the stress to concentrate in the region between the particles and results in the debonded particles at the particle-matrix interface. This process largely depends on the degree of interfacial adhesion that is attained at the particle-matrix interface. Although the growth of voids or debonding in nanoparticles may dissipate a small amount of energy, this process more importantly enables plastic void growth in the matrix to occur, which results in more dissipated energy and increases fracture resistance. For *shear banding mechanism*, the characteristics of shear banding induced by nanoparticles are similar to those observed in rubber particles. Shear bands are initiated as a result of the stress concentration in the matrix caused by the presence of the particles. Particle debonding and void growth can give rise to the localized shear banding where debonding at the particle-matrix interface can greatly reduce the degree of triaxial stresses acting on the polymer matrix next to particles. This reduction of stress enables the further growth of shear bands. Shear yielding originates from the point of maximum stress concentration, where for inorganic particles, it is at the pole of the particles.

Toughening mechanisms in epoxy-rubber composites

Like rigid inorganic fillers, rubber particles can be used to toughening epoxy resins, however, rubber particles have the ability to further enhance the toughness. The toughening mechanisms of rubber-modified epoxies have been thoroughly studied and are better understood than silica filled epoxies. Therefore, rubber toughened epoxies are commonly employed in a variety of applications. It is generally accepted in the literature that the rubber particle cavitation induced shear banding mechanisms and plastic void growth of the matrix have been found as the major toughening mechanisms. In contrast, the rubber particle bridging mechanism is only a moderate factor (see Figure 2) [36-38].

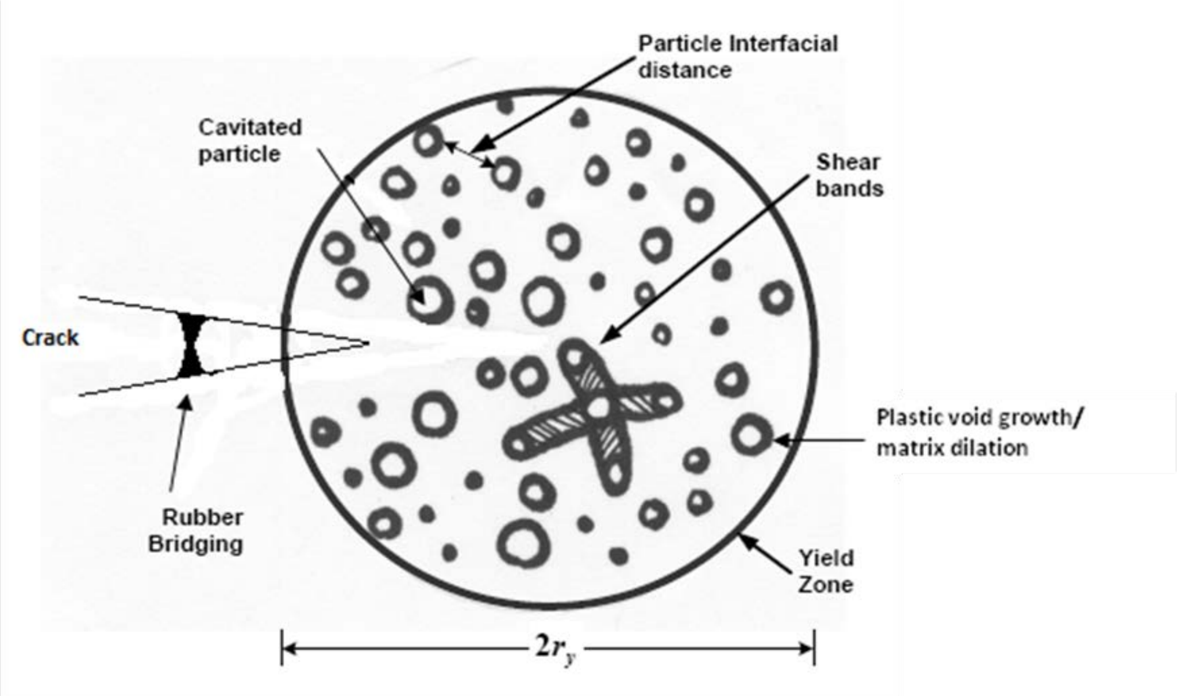


Figure 2. A Schematic drawing shows the rubber particle bridging, localized shear banding and plastic void growth. This drawing is redrawn according to Huang and Kinloch's work [33].

The role of rubber particle cavitation was ascertained by evaluating cavitation resistance with conventional rubber particles and hollow plastic particles. It was postulated that instead of a considerable contribution to strain energy adsorption, cavitation itself induces massive shear banding and matrix dilation that dissipate most amount of energy. In other words, the rubber particle cavitation triggers the matrix plastic deformation which blunts the crack tip and the matrix itself adsorbs the most strain energy during the crack propagation, consequently toughens the materials.

The size of the rubber particles will have an influence on the toughening behavior. The rubber particles tend to simply act as bridging particles given that the particle sizes are larger than the process zone size in front of the crack tip. Unlike the matrix shear banding and void growth, the rubber particle bridging will only contribute modestly to fracture toughness, and as such, larger rubber particles are less efficient in toughening epoxy resin. Moreover, it was further reported that the smaller core shell rubber particles with submicron diameters possess more toughening effectiveness.

Toughening mechanisms in hybrid epoxy-silica-rubber composites

At present, there are a limited number of studies using silica nanoparticles in rubber toughened epoxies. Due to the complicated structures involved in the systems, there is no exclusive interpretation to fully explain the toughening mechanisms in hybrid composites. Ideally, the addition of silica particles can toughen the epoxy and promote the rubber particle cavitation and shear band at the same time, resulting in considerable improvement in toughness.

The early studies for hybrid epoxy-silica-rubber composites involved micron sized silica particles, rather than nanometer sized particles. Kinloch and coworkers attributed the synergistic toughening effect to the crack pinning mechanisms. They showed that the micron sized silica particles increase the crack resistance through crack pinning mechanism in addition to the localized plastic deformation due to rubber particle [33-37]. It was also revealed that the crack pinning is the dominant mechanism in the hybrid epoxy-silica-rubber composites leading up to the crack tip blunting. The addition of micron-sized silica particles in rubber toughened epoxy can increase toughness by further enhancing the rubber cavitation/shear yielding mechanism. In addition, the process zone length in hybrid composites is also increased compared with the rubber toughened epoxy due to the synergistic toughening effect. Azimi *et al.* [38] attributed the synergy observed in fatigue crack propagation (FCP) resistance in an epoxy resin toughened by micron sized silica particles and a liquid reactive rubber. They observed that plastic deformation grows deeper into the matrix due to the stress fields associated with micron-sized silica particles. While researchers continue to investigate on the micron size scale, only a few studies have considered silica nanoparticle toward the toughening effect in a rubber toughened epoxy system. For example, addition of a small amount of silica nanoparticles applied in amino terminated butadiene acrylonitrile (ATBN) toughened epoxies results in a considerable fracture energy enhancement. However, when the nanosilica content is beyond 20 wt%, the fracture energy of the hybrid nanocomposites dramatically drops to be even lower than the fracture energy of ATBN toughened epoxy [38] as shown in Figure 3. Note that the curing condition was done at room temperature. In contrast, in a high temperature cured epoxy/anhydride system with addition of silica nanoparticles and CTBN rubber, a different toughening effect of adding silica nanopartcles was observed [5]. The fracture energy of this hybrid nanocomposite was simply proportional to the silica nanoparticle content (see Figure 4). This result suggests that curing condition should also be taken into consideration for experimental designs and comparison.

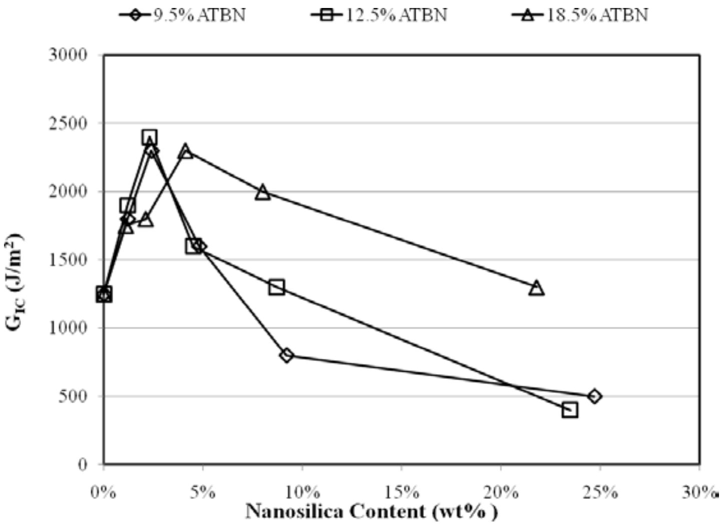


Figure 3 The fracture energy of the room temperature cured hybrid nanocomposites as a function of nanosilica content [38]

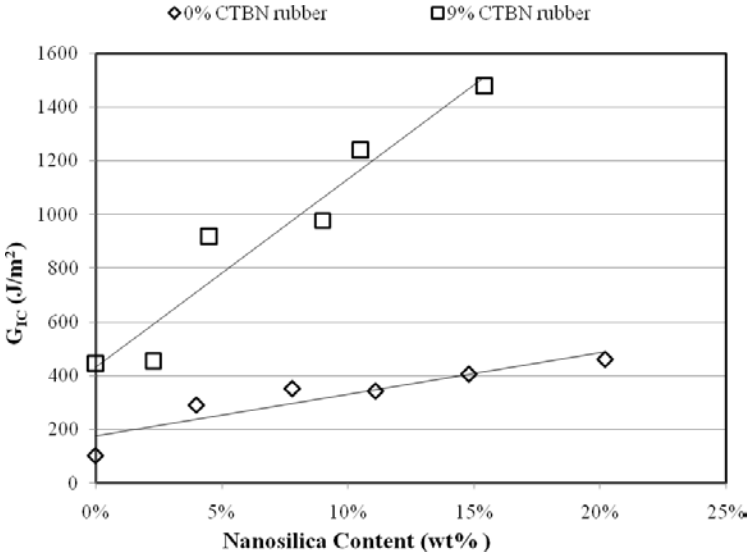


Figure 4 The fracture energy of the high temperature cured, epoxy/anhydride hybrid nanocomposites as a function of nanosilica content [5].

In conclusion, based on the literature review presented, silica nanoparticles have been investigated as a toughening agent to rubber toughened epoxies with modest success. Rubber particles mostly are based on CTBN and ATBN rubber toughened epoxies. To date, natural rubber toughened epoxies have not been reported which provides an opportunity for development and comparison to CTBN and ATBN. This research includes the use of fracture mechanics to quantify the fracture toughness, a description of toughening approaches, and an elucidation of toughening mechanisms. This work will provide the general concepts of blending silica nanoparticles in rubber toughened epoxies, and establish the basis for future developments.

Research methodology

Materials

Diglycidyl ether of bisphenol A (DGEBA, Epotec YD 535LV) was used as epoxy matrix. Cycloaliphatic polyamine (Epotec TH 7353, Aditya Birla Chemicals (Thailand) Limited) was used as the curing agent for epoxy resin. Silica nanoparticles with average particle size of 20 nm in diameter were surface modified by organosilane via a sol-gel process to prevent agglomeration and to maintain a narrow particle size distribution. The silica nanoparticles were received as predispersed in DGEBA with 40 wt% of SN (Nanopox® F 400, Evonik Industries) as shown in Fig. 5. The image shows silica nanoparticles dispersed in the epoxy matrix and confirms the particle size of silica nanoparticles to be approximately 20 nm. Epoxidized natural rubber (ENR, Epoxyprene 50, Muang Mai Guthrie Public Company Limited) containing 50 mole% of epoxide group was used as rubber toughening agent. The dissolution of ENR was conducted with toluene at the ratio of 1 g ENR per 30 cm^3 of toluene.

Composite preparation

There are three systems in this research including epoxy with ENR composites, epoxy with SN nanocomposites, and epoxy with ENR-SN hybrid nanocomposites. The formulations of all composites are shown in **Tables 1**. The designations of epoxy composites are **X**ENR-EP **Y**SN-EP and **X**ENR-**Y**SN-EP where **X** and **Y** are weight percent of ENR and SN, respectively. **X** and **Y** represent 2.5, 5.0, 7.5 and 10.0 weight percent of filler, sequentially. All formulations were carried out by mixing epoxy resin with appropriate amount of fillers to obtain desired formulation as shown in Table 1 using mechanical stirrer at 500 rpm at 110 ºC under vacuum for 24 h. After that, an appropriate amount of curing agent was added to the mixture and stirred for 10 min. The mixture was then poured to a coated Teflon aluminum mold and thermally cured at 80 °C for 1 h, followed by 150 °C for 2 h. The cured epoxy was cooled gradually to room temperature before the sample was released from mold. The samples were then cut to the desired shapes for further analysis.

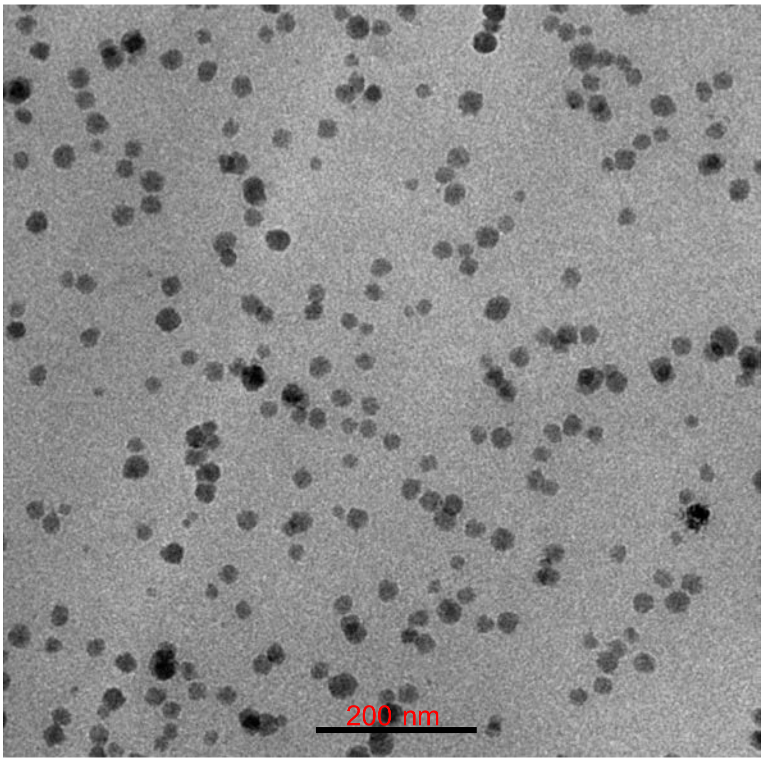


Fig. 5. TEM Micrographs of epoxy containing 5 wt% silica nanoparticles (5SN-EP).

Table 1

Formulations and designations for all composite materials.

Designations	Silica Nanoparticles (SN), wt%)	Epoxidized Natural Rubber (ENR, wt%)	Total Filler Content (wt%)
Neat Epoxy (EP)	0.0	0.0	0
2.5ENR-EP	0.0	2.5	2.5
5ENR-EP	0.0	5.0	5
7.5ENR-EP	0.0	7.5	7.5
10ENR-EP	0.0	10.0	10
2.5SN-EP	2.5	0.0	2.5
5SN-EP	5.0	0.0	5
7.5SN-EP	7.5	0.0	7.5
10SN-EP	10.0	0.0	10
5ENR-2.5SN-EP	2.5	5.0	7.5
2.5ENR-5SN-EP	5.0	2.5	7.5
5ENR-5SN-EP	5.0	5.0	10
7.5ENR-5SN-EP	5.0	7.5	12.5
5ENR-7.5SN-EP	7.5	5.0	12.5

Characterizations

The glass transition temperature (T_g) of all samples was examined by differential scanning calorimeter (METTLER TOLEDO DSC1). Samples of approximately 8-10 mg were used, and the testing protocol followed ramping from 25 °C to 200 °C under nitrogen gas with heating rate of 10 °C/min. All the tests were run twice, and the values of T_g were reported from the second scan.

The Young's modulus (E) and yield stress (σ_y) were measured using universal tensile testing machine (COMETECH B1 TYPE). All the samples are machined into a dog-bone shape, 63.5 mm in length, 3 mm gage section width, and 3 mm in thickness for the tensile testing. At least five dog-bone samples were tested at the crosshead speed of 5 mm/min at room temperature, according to the ASTM D638 standard test method (type V) [9].

Fracture toughness (K_{IC}) was measured using single-edge notch three-point-bending (SEN3PB) type specimen, and the tests were performed by universal tensile testing machine (COMETECH B1 TYPE) in accordance to the ASTM D5045 standard. A pre-crack was made by tapping a fresh razor blade between the adjoining plates. At least five single-edge-notched specimens with dimension of 76.2 mm x 12.7 mm x 6.4 mm were tested at a rate of 1 mm/min, and the span was set as 50.8 mm. The K_{IC} of all composites was calculated by the following equation [32].

$$K_{IC} = Y \frac{6P_fS}{4tw^2}\sqrt{a}$$

where Y is the shape factor, P_f is the load at the break, S is the length of the span (50.8 mm), w is the width of the sample, t is the thickness of the sample, and a is the crack length.

The fracture surfaces for all hybrid nanocomposites were investigated by a scanning electron microscopy (SEM-EDS, JEOL JSM-7600F). The samples were coated with a thin layer of sputtered platinum prior to analysis. Voltages of 5 kv and 15 kv were used for SEM and EDS analysis, respectively.

The dispersion and size of silica nanoparticles dispersed in epoxy matrix were performed by transmission electron microscopy (120 kv, TEM-Hitachi HT7700). The samples were cut using cryo-microtomed technique under -10 °C to obtain a thin layer of approximately 60-100 nm before examination.

Result and Discussion

1. Particle dispersion

Fig. 6 shows the SEM-EDS micrographs of epoxy resins containing SN, ENR, and mixture of both. The Images shows silica nanoparticles are well dispersed in the epoxy matrix and confirms that addition of ENR into epoxy containing SN particles did not affect the particle. Therefore, the curing procedures used in this work produced epoxy-ENR-SN systems with uniform dispersions.

2. Glass transition temperature (T_g)

The glass transition temperatures of neat epoxy and epoxies containing silica nanoparticles, epoxidized natural rubber, and mixture of both are presented in Table 2. The T_g of neat epoxy resin was determined to be 119.5 ^{o}C. For single component SN filler system, the addition of SN was found to slightly increase the T_g of epoxy, however, the effect of SN content within the range of 0-10 wt% is no impact and the T_g values for all the SN-epoxy composites were found to be within 124±1 ^{o}C. The increase in T_g can be attributed to a more restriction of polymer chain mobility caused by SN addition into epoxy system. On the other hand, for single component ENR filler system, the T_g was found to decrease by approximately 15 ºC and continue to decrease with increasing ENR content. The decrease in T_g values of epoxy resin is due to the chain flexibility of ENR and is consistently with literature [33].

For this new hybrid nanocomposites, a decrease in T_g was also observed for all hybrid formulations compared the neat resin, as shown in Table 2. This observation is not surprising since the hybrid systems contain the flexible chains of ENR. Therefore, the decrease in T_g values can be expected. With increasing amount of ENR in the hybrid system at fixed SN content, the values of T_g were found to decrease. However, with increasing amount of SN at fixed ENR content represents shows modest effect on the T_g of hybrid nanocomposites. Since the T_g is related to the level of free volume in polymer matrix and the polymer chain mobility, the addition of ENR and SN in the epoxy matrix causes small change of the chain mobility of the epoxy/cycloaliphatic polyamide matrix [7]. From the current results, the synergy with SN and ENR to the hybrid synergy in term of Tg was observed and the addition of SN and ENR induces a scattering effect on the T_g of hybrid nanocomposites in a range of ±6 ºC. With addition of SN to the epoxy containing only ENR, the Tg was dominated and found be higher compared with the epoxy containing only ENR.

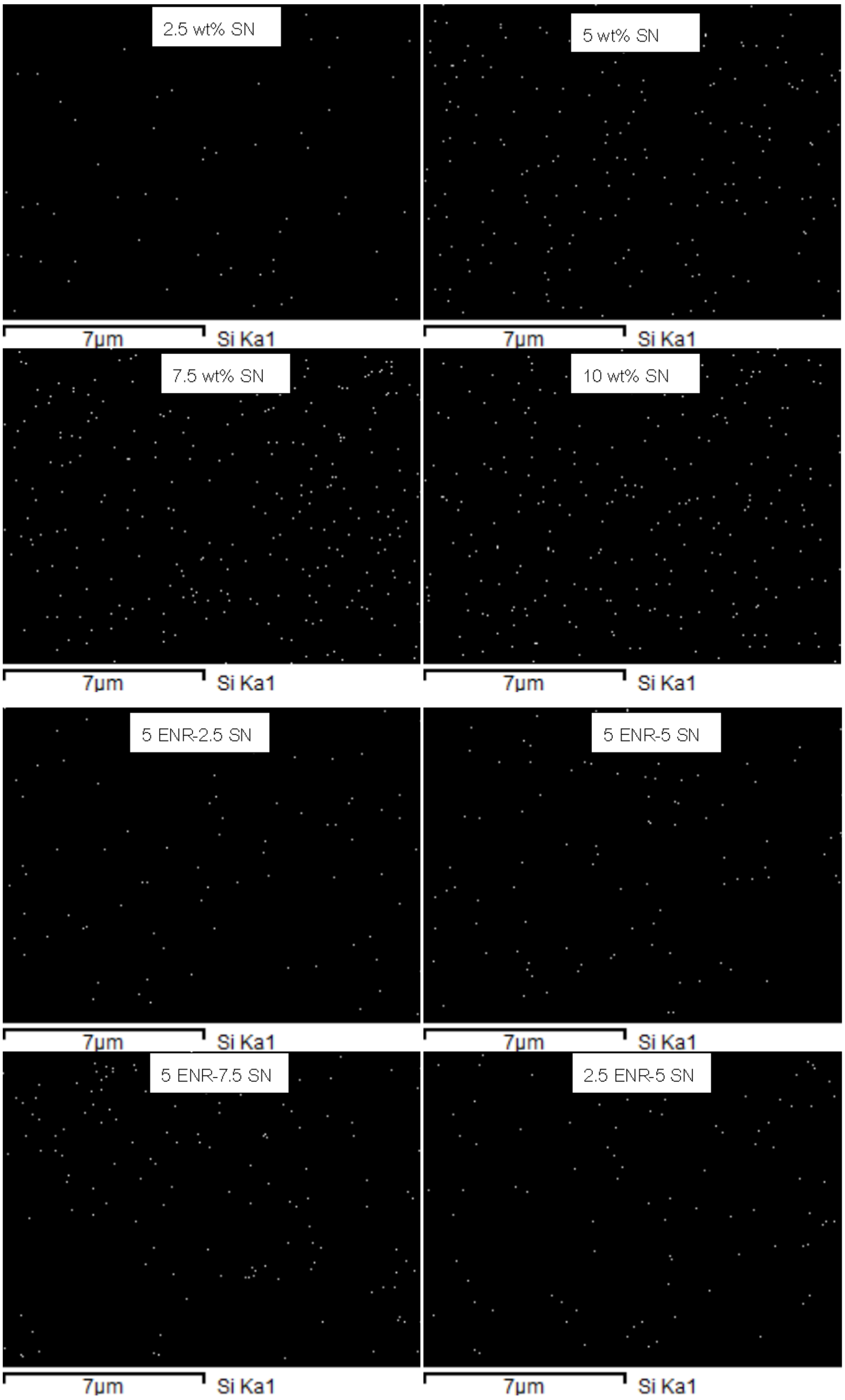


Fig. 6 SEM-EDS micrographs of epoxy containing SN and mixture of SN and ENR.

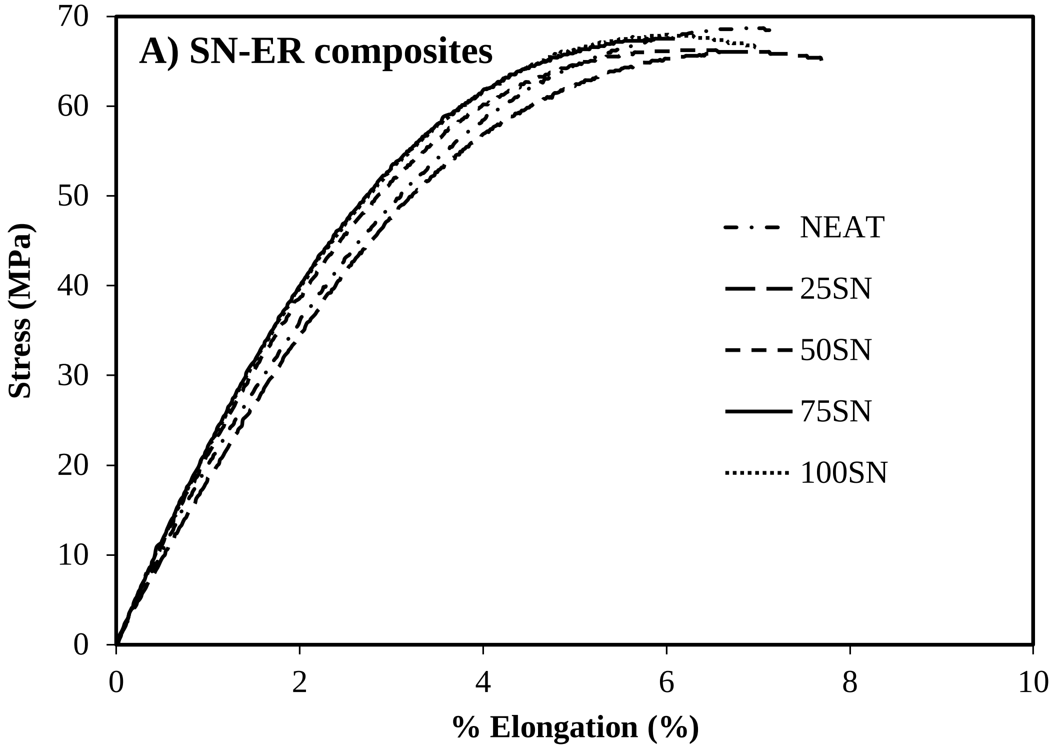
Table 2 Values of Glass transition temperatures, yield stress, Young's modulus, and fracture toughness of epoxy containing single components and hybrid nanocomposites, compared at different filler contents.

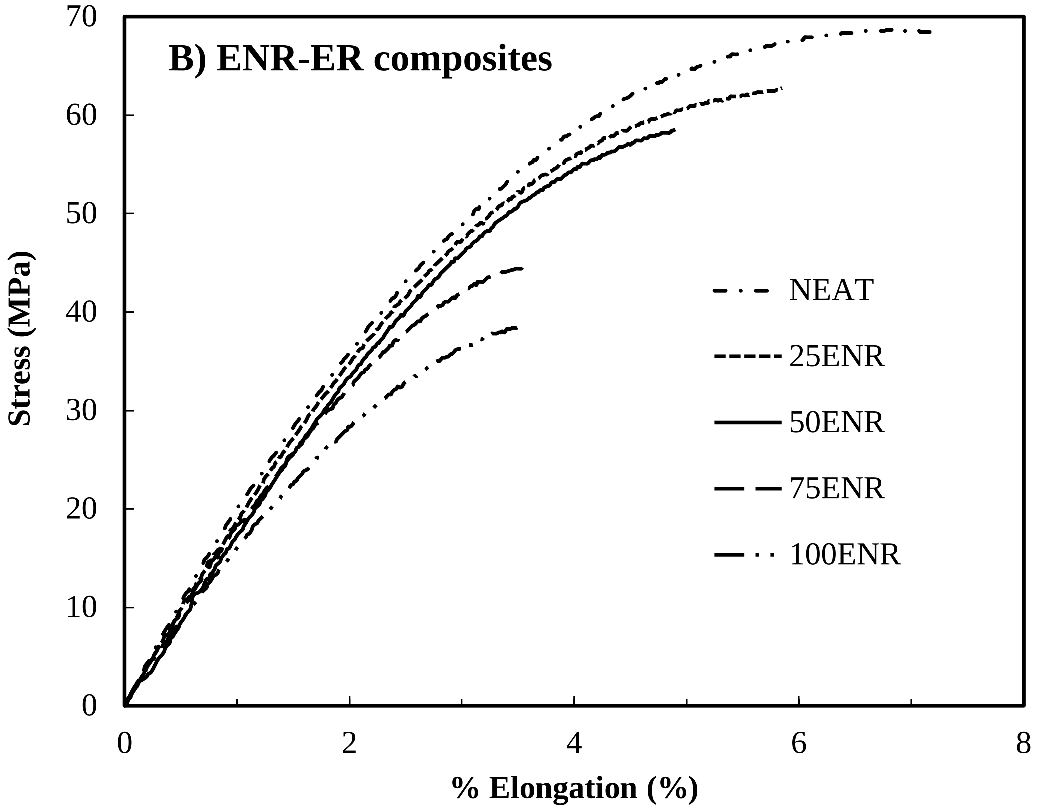
Epoxy Formulations	T_g (^oC)	Yield strength (MPa)	E (GPa)	K_{IC} (MPa/m^2)
Neat EP	119.5	66.2±3.5	2.25±0.05	0.88±0.01
Single component ENR				
2.5ENR-EP	105.0	56.7±1.0	2.02±0.14	1.69±0.03
5.0ENR-EP	103.6	52.9±1.8	1.90±0.06	1.70±0.04
7.5ENR-EP	102.6	45.1±1.3	1.84±0.07	2.07±0.04
10.0ENR-EP	96.9	37.8±2.4	1.78±0.05	2.05±0.07
Single component SN				
2.5SN-EP	124.7	65.5±2.2	2.30±0.10	1.04±0.03
5.0SN-EP	124.8	65.7±1.0	2.54±0.04	1.16±0.08
7.5SN-EP	123.4	66.9±1.5	2.66±0.04	1.21±0.02
10.0SN-EP	124.3	70.0±3.2	2.71±0.10	1.33±0.05
Hybrid nanocomposites				
2.5ENR-5.0SN-EP	110.3	62.7±0.6	2.58±0.04	1.64±0.04
5.0ENR-5.0SN-EP	105.5	60.3±1.2	2.37±0.02	2.00±0.03
7.5ENR-5.0SN-EP	103.0	45.4±0.7	2.31±0.01	2.09±0.04
5.0ENR-2.5SN-EP	106.8	56.1±0.6	2.31±0.02	2.03±0.03
5.0ENR-7.5SN-EP	107.8	62.8±1.2	2.61±0.03	1.78±0.04

3. Yield strength σ_y and Young's modulus (E)

The tensile behavior of composite materials is shown in Fig.7. Fig. 7 shows that all composite materials are a rigid and brittle with low elongation at break of 1-2%. For the epoxy containing single fillers, the material breaks after yield without necking. The addition of SN and ENR in the epoxy matrix changed the brittle fracture of epoxy resins to a ductile fracture as shown in Fig. 2C

The results for the yield strength of the single component and hybrid epoxies are shown in Table 2 and Fig. 8. For single filler SN systems, the addition of SN does not significantly increase the σ_y of epoxy resin. This result is consistent with previous literatures [34-35], reporting that the additional failure mechanisms introduced by silica nanoparticles effectively prevent matrix deformation and do not affect the σ_y. For single filler ENR systems, the σ_y of epoxy was found to significantly decrease with increasing of ENR content. The contributions from flexible chain and the low T_g of ENR are responsible for the decrease in σ [5]. For the hybrid nanocomposites, the σ was found to decrease for all filler combinations compared to the neat epoxy as shown in Table 2. However, when comparing the σ_y of hybrid systems to that of single filler systems at the same total wt% of fillers, as presented in Fig. 3, the addition of SN particles to epoxy containing 5wt% ENR had shown an improvement in σ_y. The contribution from ENR has shown significant impact on the σ_y of hybrid nanocomposites. To explain the phenomenon, the degree of the interfacial strength between fillers and polymer matrix should be considered . When polymer materials are filled particles, an interfacial layer will be formed between inclusions and the matrix. The yield strength is not only affected by the degree of the interfacial strength between particle and polymer matrix but also to properties of the matrix materials (e.g. ductile or brittle) of the fillers. For the systems with poor filler-matrix interfacial adhesion, the strength of a composite is determined by the effective available area of load-bearing matrix in the absence of the filler. In this case, the polymer matrix partially contains flexible ENR, therefore the SN particles cannot effectively transfer the stress to the polymer matrix. Thus, the yield strength of the hybrid nanocomposites was observed to decrease for all the formulations. However, compared to epoxy containing only the single ENR at same total wt%, it can be seen that the yield strength of the hybrid composites with a mixture of SN and ENR have a modest but consistently higher yield compared to that of ENR counterparts.


A) SN-ER composites
NEAT
25SN
50SN
75SN
100SN
Stress (MPa)
0
10
20
30
40
50
60
70
% Elongation (%)
0
2
4
6
8
10


B) ENR-ER composites
NEAT
25ENR
50ENR
75ENR
100ENR
Stress (MPa)
0
10
20
30
40
50
60
70
% Elongation (%)
0
2
4
6
8

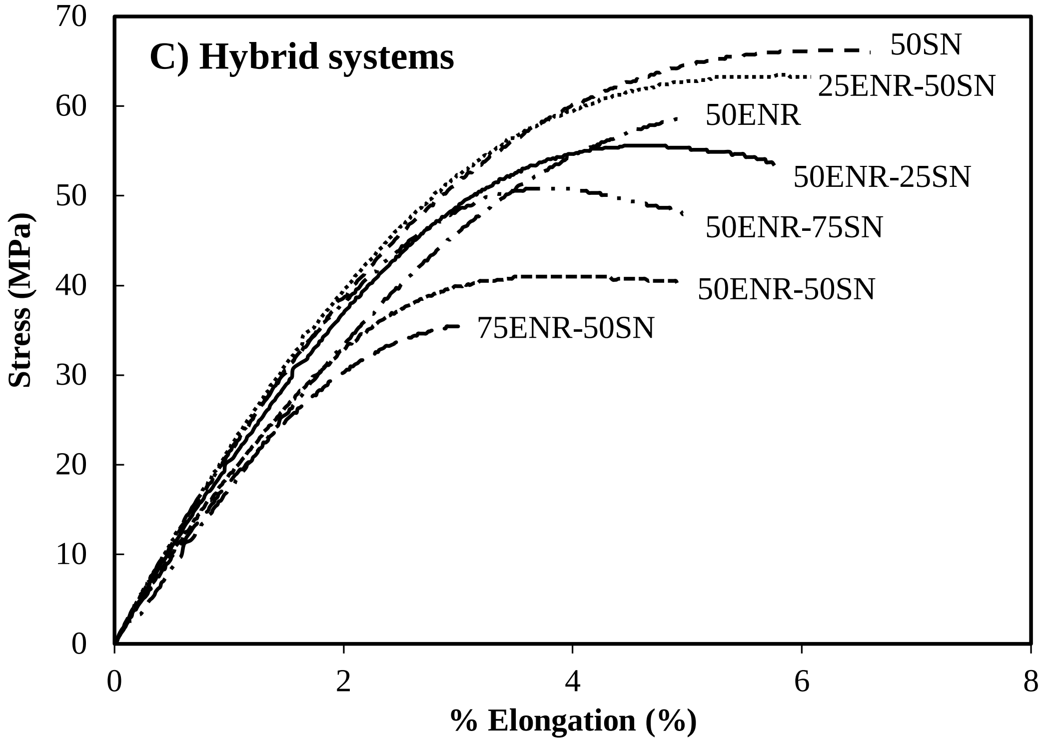


Figure 7. Tensile behavior of epoxy nanocomposites for A) SN single component B) ENR single component, and C) SN and ENR hybrid systems.

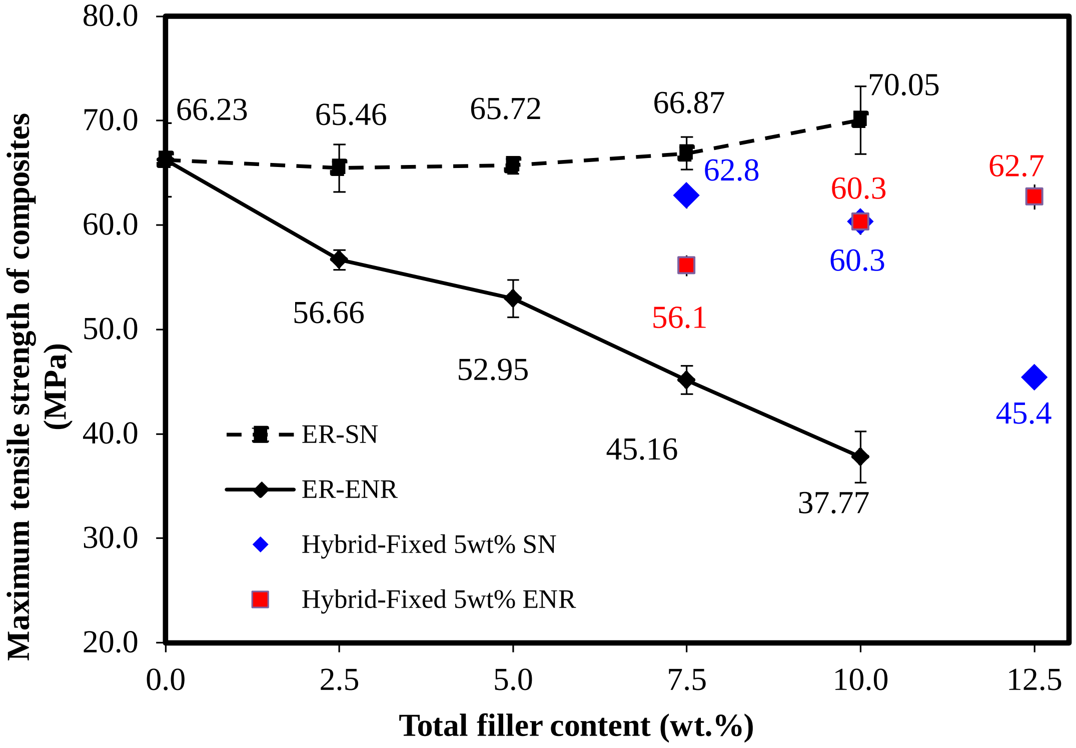


Figure 8. Yield strength of composites versus total filler content. For single filler component system, dashed line represents epoxy resin filled with various SN contents. Solid line represents epoxy resin filled with various ENR contents. For hybrid systems, fracture toughness of hybrid nanocomposites is plotted against total filler content (wt% of SN+ENR). Red dot represents epoxy resin filled with fixed 5 wt% ENR at various SN contents. Blue dot represents epoxy resin filled with fixed 5 wt% SN at various ENR contents.

The Young’s moduli of epoxy containing single component and hybrid component were measured using dog-bone shaped tensile specimens, shown in Table 2 with the standard deviations. For epoxy containing SN, the increase in the Young’s modulus for epoxy filled SN relative to unmodified epoxy is clearly observed. The Young’s modulus of epoxy resin steadily increases with filler content, from 2.25 GPa (neat resin) to the highest value of 2.71 GPa (10wt% of SN). This increase is due to a much higher modulus of silica nanoparticles (~70 GPa) compared to the neat resin [7]. On the other hand, the Young’s modulus of epoxy containing ENR was found to decrease with increasing of ENR content. The results are consistent with observations for similar systems that the decrease in *E* can be attributed from the flexible chain and the low T_g of ENR [32, 6].

The Young’s moduli of hybrid nanocomposites are also shown in Table 2 and Fig.9. The increase in the E for these hybrid nanocomposites relative to unmodified epoxy is clearly observed. For example, the addition of 2.5 wt% ENR into epoxy containing 5wt% SN was found to increase the *E* values. With increasing ENR content, the *E* of composites continues to decrease. The highest E’s value of 2.63 GPa was found at 2.5 wt% ENR and 5wt% SN. On the other hand, addition of 2.5 wt% SN in epoxy containing 5 wt% ENR was also found to improve *E*. Furthermore, by increasing the SN content into epoxy containing fixed 5 wt% ENR, the *E* continue to improve. The highest E’s value of 2.60 GPa was found at 7.5 wt% SN and 5wt% ENR. The contribution of SN for improved E of hybrid nanocomposites is clearly shown. The enhancement in stiffness of the hybrid composite can be explained by the strong interfacial bond strength between fillers and the polymer matrix, contributed from the SN, that allows efficient stress transfer from the matrix to the particles. Additionally, SN have much higher modulus of ~70 GPa than that of epoxy matrix, therefore, the stresses are effectively transferred to the interface, resulting in increased stiffness.

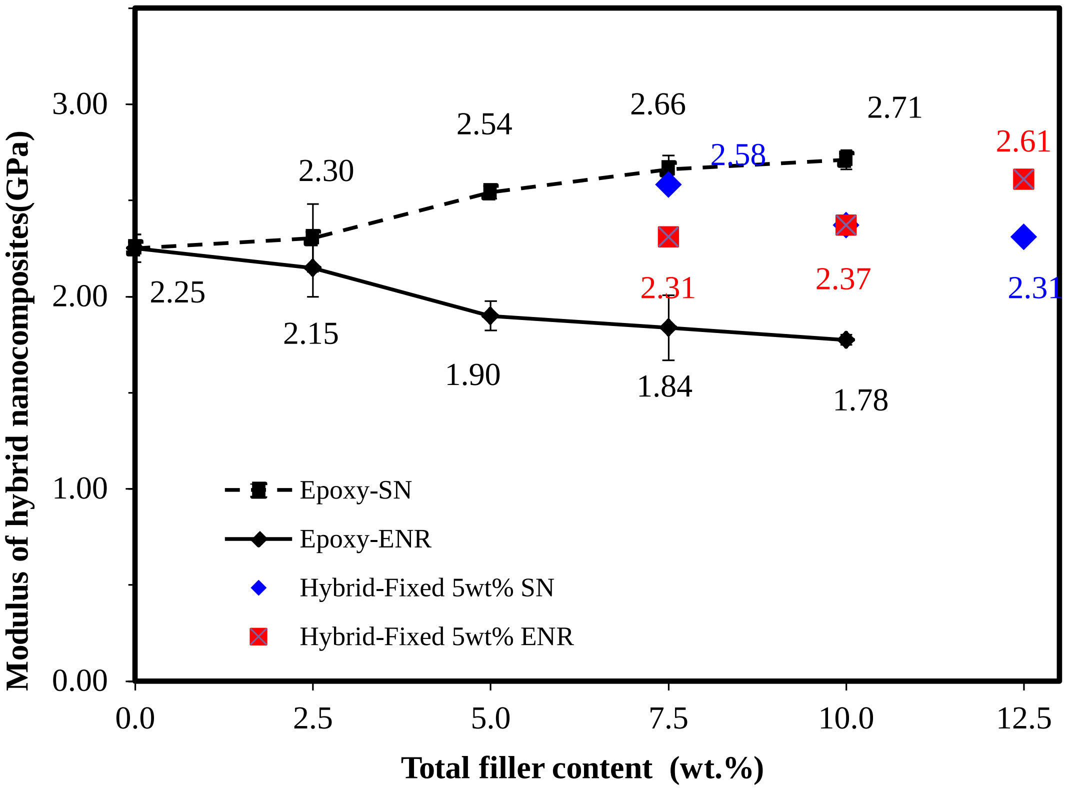


Figure 9. Moduli of hybrid nanocomposites versus total filler content. For single filler component systems, dashed line represents epoxy resin filled with various SN contents. Solid line represents epoxy resin filled with various ENR contents. For hybrid systems, fracture toughness of hybrid nanocomposites is plotted against total filler content (wt% of SN+ENR). Red dots represents epoxy resin filled with fixed 5 wt% of ENR at various SN contents. Blue dots represents epoxy resin filled with fixed 5 wt% of SN at various ENR contents.

3. Fracture toughness

The results for the fracture toughness of epoxy containing only ENR or SN and epoxy containing mixture of ENR-SN are shown in Table 2 and Fig.10. As shown in Table 2, the addition of ENR into epoxy matrix resulted in significant improvement of K_{IC} compared to neat epoxy. The %improvement in K_{IC} values of epoxy containing ENR at 2.5, 5.0, 7.5 and 10.0 wt% of ENR compared to neat resins, are 92%, 101%, 131% and 111 %, respectively. The highest K_{IC} value of 2.03 MPa/m^2 values were found at epoxy containing ENR 7.5 wt%. The addition of SN into epoxy resulted in a subtle K_{IC} improvement when compared with epoxy containing ENR. The % increase in K_{IC} of epoxy containing SN compared with the neat resin were a modest 18, 24, 28 and 40% improvement with increasing amount of 2.5, 5.0, 7.5 and 10.0 wt% SN, respectively.

For the hybrid nanocomposites, the fracture toughness was also improved when mixtures of silica nanoparticles and rubber particles were introduced in the epoxy matrix, as depicted in Fig. 10. The dashed line represents epoxy resin filled with various SN contents and solid line represents epoxy resin filled with various ENR contents. Interestingly, the addition of a few weight percent SN to an ENR toughened epoxy can lead to a more than doubling of the K_{IC} value for all hybrid composite formulations. The % improvement in K_{IC} of hybrid nanocomposites compared with neat epoxy was calculated to be in a range of 110 to 131 %. In this study, the highest K_{IC} was found at epoxy containing 7.5 wt% SN and 5 wt% ENR. Compared to the single filler system at same total wt%, it can be seen that the K_{IC} of the hybrid nanocomposites with a binary mixture of ENR and SN have a modest but consistently higher fracture toughness compared to that of the single component counterparts.

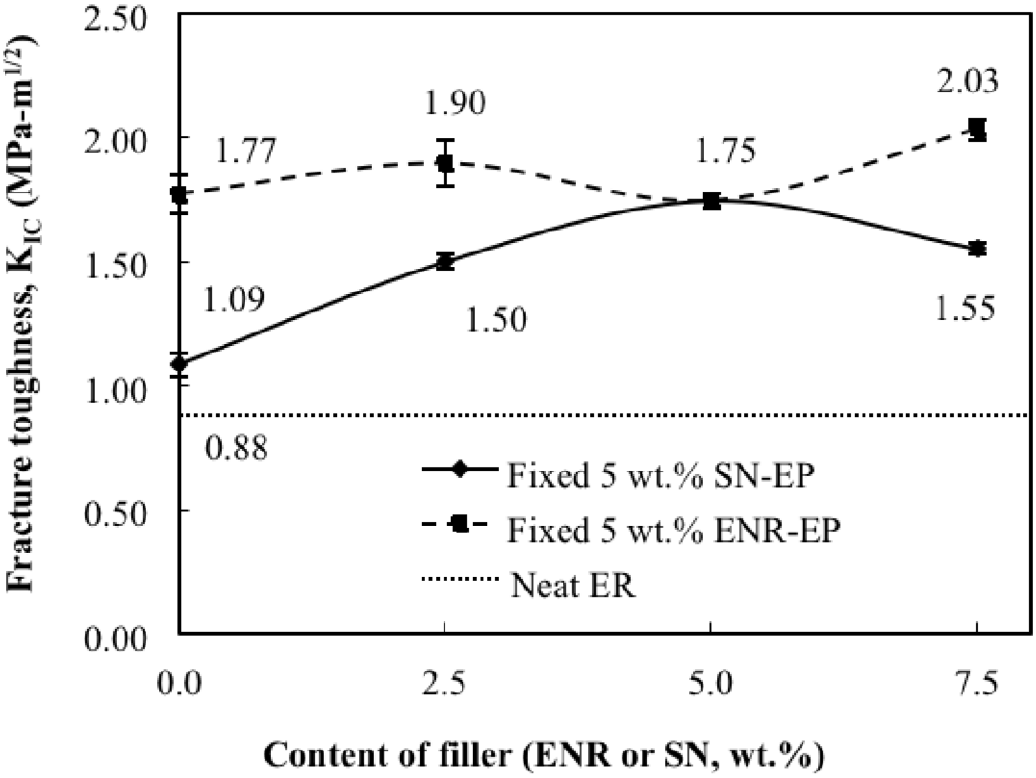


Figure 10. Fracture toughness of hybrid nanocomposites versus filler content. Dashed line represents epoxy resin filled with fixed 5 wt% of ENR at various SN contents. Solid line represents epoxy resin filled with fixed 5 wt% of SN at various ENR contents. For reference, dotted line represents K_{IC} of neat epoxy resin.

4. Toughening Mechanisms

The improvements in toughness were visually explored using scanning electron microscopy (SEM). Fig. 11a-d show SEM images of fracture surfaces of SEN3PB specimens near the precrack region of epoxies containing was 0-10wt% of ENR. The arrows shown on the upper left of the images indicate the crack propagation. The presence of rubber cavitation was observed for all epoxy containing ENR. The rubber cavitation is associated with stress fields generating dilation that can cause failure and void formation inside the particles. These void growth are created due to a much lower modulus of rubber particles compared to that of epoxy resin. Therefore, the toughness improvements in rubber-toughened polymers were due to the particle cavitation of rubber particles [36-38]. The rubber particle sizes were measured to be in the range of approximately 1-3 microns and amount of rubber cavitation increased steadily with ENR concentration. These results are correlated with the fracture toughness results where as the concentration of ENR increases, the K_{IC} value also increases.

The SEM fracture surfaces of epoxy containing SN particles are also shown in Fig. 11e-f. The presence of the surface roughness and particle debonding caused by SN were observed as shown in Fig. 12e and 12f, respectively. The nanoparticles are hard to detect using the SEM, however, particle debonding of similar particle size has been observed in literature for 20 nm filled DGEBA systems [22]. This SN debonding mechanism was found to be similar to the particle cativation mechanism found in rubber-toughened epoxies. In silica particles, the plastic void growth is initiated by debonding of the particles, causing failure and void formation at the particle –matrix interface. Since the SN have a much higher modulus than the matrix, cavitation or voids occur around the particle at the particle-matrix interface. In rubber particles, these voids are created internally. These observations indicates that debonding of nanoparticles allows the energy to dissipate via the plastic void growth mechanism; which are responsible for the increase in fracture toughness of epoxy systems.

For the hybrid nanocomposites as shown in Fig. 12a-f, rubber cavitation mechanism is clearly observed on the fracture surfaces for all hybrid systems. For the toughening contribution from SN, the particle debonding is hard to detect, however, there is an evidence of surface roughness observed on the fracture surface especially at high concentration of SN as shown in Fig. 12e. In addition, Fig. 12d and 12e present epoxy containing 5 wt% ENR+2.5wt% SN, and 5wt% ENR+7.5wt% SN, respectively. It clearly shows that the size of the voids created from the rubber particles with presence of higher concentration SN particles was larger than that of lower concentration of SN particles. A possible explanation is that the presence of SN particles may increase the ductility of the epoxy matrix around the ENR particles and facilitate the particle cavitation, which simply increase the fraction of epoxy matrix that has plastically deformed. This result also suggests that the matrix-particle adhesion strength decreases with the addition of SN particle. In addition, the yield strength usually decreases with poor of matrix-particle adhesion. For the current system, yield strength is found to decrease for all the hybrid systems, therefore, it is likely that the SN addition causes a weaken matrix-particle. The combination of SN with ENR particles can lead to materials that are tougher than using either type of reinforcing agents alone.

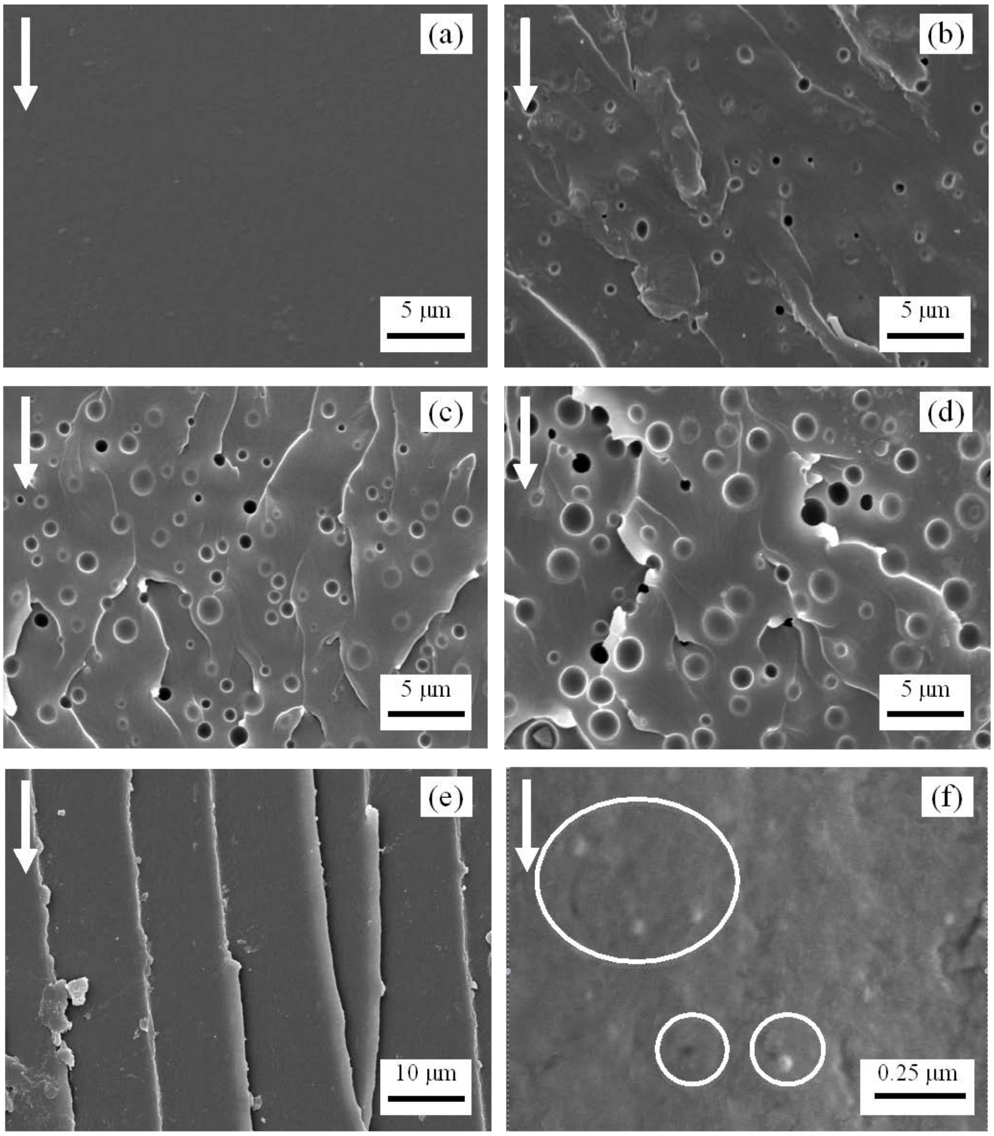


Figure 11. SEM Micrographs of fracture surfaces of single systems; (a) Neat epoxy, (b) 5ENR-EP, (c) 7.5ENR-EP, (d) 10ENR-EP, (e) 5SN-EP, and (f) 10SN-EP.

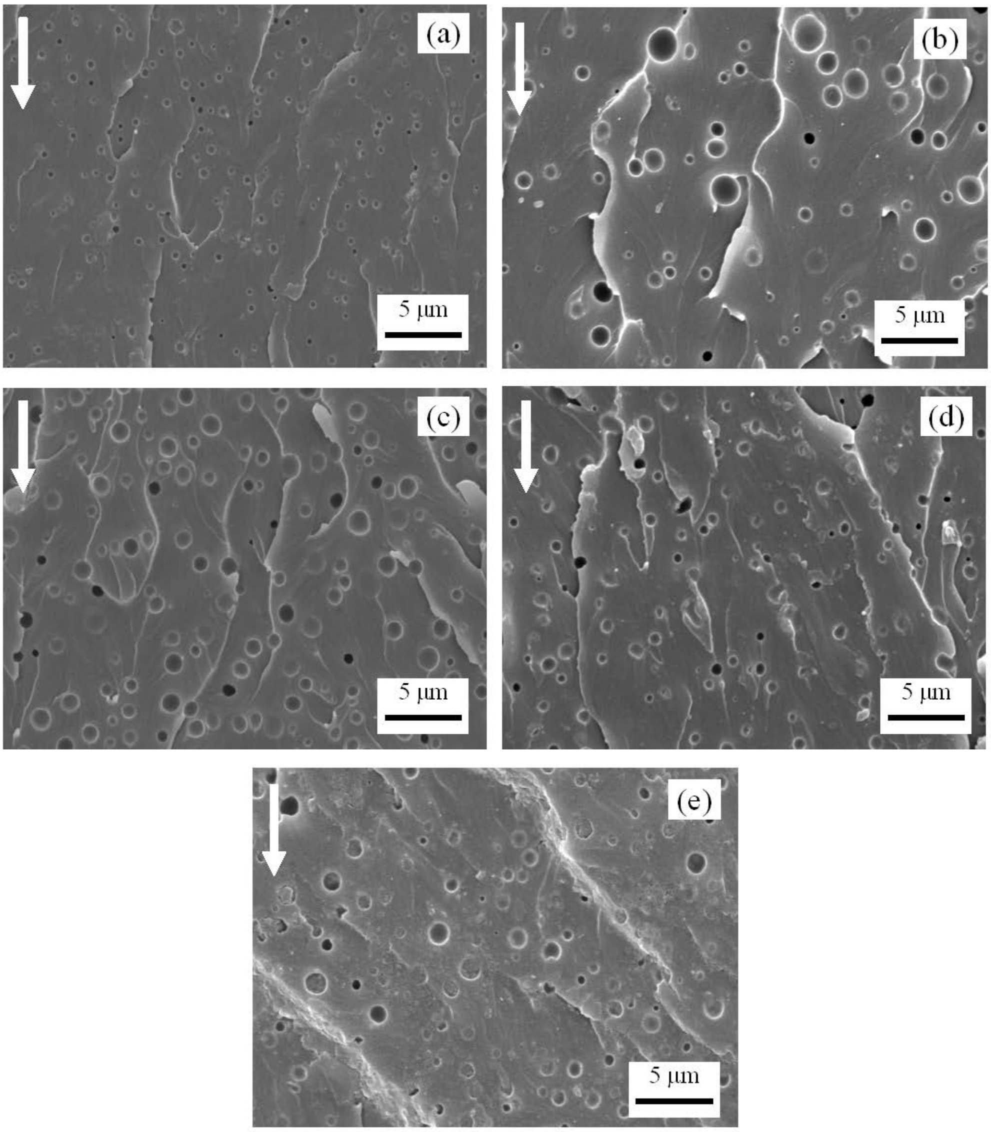


Figure 12. SEM Micrographs of fracture surfaces of hybrid nanocomposites; (a) 2.5ENR-5SN-EP, (b) 5ENR-5SN-EP, (c) 7.5ENR-5SN-EP, (d) 5ENR-2.5SN-EP, and (e) 5ENR-7.5SN-EP.

In summary, the mixture of SN and ENR can be successfully used as toughening agents while maintaining or improving the initial properties of epoxy resins. The initial properties maintained include high Tg and high Young's modulus, which are basic requirements of properties for good adhesives or materiasl for high performance applications such as aerospace and electronic devices. In addition, the results from the current investigation provide evidence of particle debonding of nanoparticles and particle cavitation contributed from silica nanoparticles and rubber particles, respectively, as the major toughening mechanisms in hybrid epoxy systems.

Fig. 13 presents the schematic progression of the specimen fracture for ENR-EP system, SN-EP systems, and ENR-SN hybrid system. For ENR-EP systems, particle cavitation of rubber particles were observed while particle debonding mechanism was observed for SN-EP systems. For hybrid systems, particle debonding and cavitation mechanisms were observed and are attributed to be responsible for the toughness improvements for epoxy. The presence of SN particles may increase ductility of the epoxy matrix around the ENR particles and facilitate the particle cavitation. The synergistic toughening mechanism can be observed by fracture roughness on specimen surface.

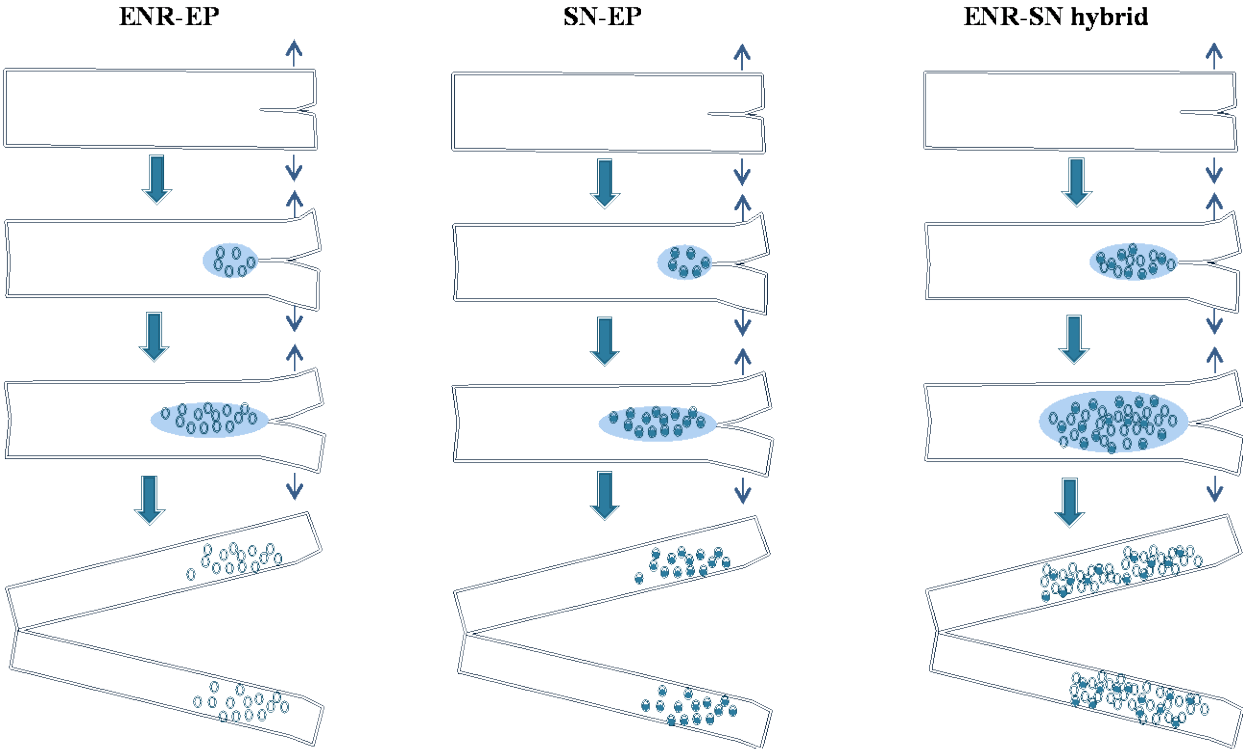


Figure 13. Progression of a specimen fracture and toughening mechanisms for ENR-EP system (circle representing particle cavitation), SN-EP systems (filled dot and circle presenting particle debonding with void growth), and ENR-SN hybrid system.

Conclusions

An approach in toughening and improving mechanical properties of epoxy resins by rubbers and silica particles was studied, as single component systems and hybrid systems. Epoxy matrix consisted of standard diglycidyl ether of bisphenol A resin (DGEBA). The silica nanoparticles with the particle size of approximately 20 nm were used, and epoxidized natural rubber was used as a second filler in the epoxy matrix. For single component systems, it was revealed that the addition of ENR resulted in the reduction in the T_g and modulus of epoxy resins, whereas the addition of SN resulted in slightly increased values of T_g and significant improvement in the modulus. However, the enhancement in both T_g and the Young's modulus for hybrid ENR-SN nanocomposites were observed. Interestingly, the addition of a few weight percent SN to an ENR toughened epoxy can lead to a doubling of the K_{IC} value. The improvements in toughness were visually evidenced using scanning electron microscopy. Particle cavitation of rubber particles and particle debonding of silica nanoparticles were observed and are attributed to be responsible for the toughness improvements for epoxy. The presence of SN particles may increase ductility of the epoxy matrix around the ENR particles and facilitate the particle cavitation, which simply increase the fraction of epoxy matrix that has plastically deformed.

References

1. H. Lee and K. Neville, *Handbook of Epoxy Resins*. 1967: McGraw-Hill.
2. S.H. Goodman, *Handbook of Thermoset Plastic*. 1986: Noyes.
3. C. May, *Epoxy Resins Chemistry and Technology*. 1988: Marcel Dekker Inc.
4. P. Ruamcharoen, S. Umaree, and J. Ruamcharoen, *Relationship between Tensile Properties and Morphology of Epoxy Resin Modified by Epoxidised Natural Rubber.* Journal of Materials Science and Engineering, 2011. **5**: p. 504-510.
5. Y. L. Liang and R.A. Pearson, The toughening mechanism in hybrid epoxy-silica-rubber nanocomposites (HESRNs). Polymer, 2010. **51**(21): p. 4880-4890.
6. S. Chuayjuljit, N. Soatthiyanon, and P. Potiyaraj, *Polymer blends of epoxy resin and epoxidized natural rubber.* Journal of Applied Polymer Science, 2006. **102**(1): p. 452-459.
7. P. Dittanet and R.A. Pearson, Effect of silica nanoparticle size on toughening mechanisms of filled epoxy. Polymer, 2012. **53**(9): p. 1890-1905.
8. P. Dittanet, Fracture Behavior of Silica Nanoparticle Filled Epoxy Resin, in Polymer Science and Engineering. 2011, Lehigh University: Bethlehem, PA.

9. P. Dittanet and R.A. Pearson, Effect of bimodal particle size distributions on the toughening mechanisms in silica nanoparticle filled epoxy resin. Polymer, 2013. **54**(7): p. 1832-1845.

10. P.P. Vijayan, et al., Liquid rubber and silicon carbide nanofiber modified epoxy nanocomposites: Volume shrinkage, cure kinetics and properties. Composites Science and Technology, 2014. **102**: p. 65-73.

11. S. K. Tan, et al., A Comparison Study of Liquid Natural Rubber (LNR) and Liquid Epoxidized Natural Rubber (LENR) as the Toughening Agent for Epoxy. American Journal of Materials Science, 2013. **3**(3): p. 55-61.

12. B. B. Johnsen, et al., Toughening mechanisms of nanoparticle-modified epoxy polymers. Polymer, 2007. **48**(2): p. 530-541.

13. D. Quan and A. Ivankovic, Effect of core–shell rubber (CSR) nano-particles on mechanical properties and fracture toughness of an epoxy polymer. Polymer, 2015. **66**: p. 16-28.

14. M. Preghenella, a. Pegoretti, and C. Migliaresi, *Atomic force acoustic microscopy analysis of epoxy-silica nanocomposites.* Polymer Testing, 2006. **25**: p. 443-451.

15. H. Yahyaie, et al., *Toughening mechanisms of rubber modified thin film epoxy resins.* Progress in Organic Coatings, 2013. **76**(1): p. 286-292.

16. R.A. Sharma, et al., *Effect of Nano/micro Silica on Electrical Property of Unsaturated Polyester Resin Composites.* Transactions on Electrical and Electronic Materials, 2012. **13**(1): p. 31-34.

17. B.M. Novak, Hybrid Nanocomposite Materials-between inorganic glasses and organic polymers. Advanced Materials, 2004. **5**(6): p. 422-433.

18. M.H. Blees, et al., The effect of friction on scratch adhesion testing: application to a sol-gel coating on polypropylene. Thin Solid Films, 2000. **359**: p. 1-13.

19. S. El-Sayed, et al., Effect of nanosilica on optical, electric modulus and AC conductivity of polyvinyl alcohol/polyaniline films. Physica B: Condensed Matter, 2015. **464**: p. 17-27.

20. Y. L. Liang and R. A. Pearson, *Toughening mechanisms in epoxy–silica nanocomposites (ESNs).* Polymer, 2009. **50**(20): p. 4895-4905.

21. H. Zhang, et al., Fracture behaviours of in situ silica nanoparticle-filled epoxy at different temperatures. Polymer, 2008. **49**(17): p. 3816-3825.

22. H. Zhang, et al., Property improvements of in situ epoxy nanocomposites with reduced interparticle distance at high nanosilica content. Acta Materialia, 2006. **54**(7): p. 1833-1842.

23. B. Lauke, *On the effect of particle size on fracture toughness of polymer composites.* Composites Science and Technology, 2008. **68**(15–16): p. 3365-3372.

24. C. L. Hsieh and W. H. Tuan, *Thermal expansion behavior of a model ceramic–metal composite.* Materials Science and Engineering: A, 2007. **460–461**: p. 453-458.

25. B.B. Johnsen, A.J. Kinloch, and A.C. Taylor, Toughness of syndiotactic polystyrene/epoxy polymer blends: microstructure and toughening mechanisms. Polymer, 2005. **46**(18): p. 7352-7369.

26. H. Ismail, S. Tan, and B.T. Poh, *Curing and Mechanical Properties of Nitrile and Natural Rubber Blends.* Journal of Elastomers and Plastics, 2001. **33**(4): p. 251-262.

27. H. Ismail, S.M. Shaari, and N. Othman, The effect of chitosan loading on the curing characteristics, mechanical and morphological properties of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) compounds. Polymer Testing, 2011. **30**(7): p. 784-790.

28. A.G. Margaritis, J.K. Kallitsis, and N.K. Kalfoglou, Miscibility of chlorinated polymers with epoxidized natural rubber: 3. Blends with chlorinated polyethylenes. Polymer, 1987. **28**: p. 2122-2129.

29. N. Z. Noriman, H. Ismail, and A.A. Rashid, Characterization of styrene butadiene rubber/recycled acrylonitrile-butadiene rubber (SBR/NBRr) blends: The effects of epoxidized natural rubber (ENR-50) as a compatibilizer. Polymer Testing, 2010. **29**(2): p. 200-208.

30. N. Chikhi, S. Fellahi, and M. Bakar, *Modification of epoxy resin using reactive liquid (ATBN) rubber.* European Polymer Journal, 2002. **38**(2): p. 251-264.

31. S. Sprenger, M.H. Kothmann, and V. Altstaedt, Carbon fiber-reinforced composites using an epoxy resin matrix modified with reactive liquid rubber and silica nanoparticles. Composites Science and Technology, 2014. **105**: p. 86-95.

32. R.W. Hertzberg, R.P. Vinci, and J.L. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*. 2012: John Wiley & Sons.

33. A.J. Kinloch, R.D. Mohammed, and A.C. Taylor, The Effect of Silica Nano-Particles and Rubber Particles on the Toughness of Multiphase Thermosetting Epoxy Polymers. Materials Science, 2005. **40**: p. 5083-86.

34. Y. Sun, Z. Zhang, and C.P. Wong, *Study on mono-dispersed nano-size silica by surface modification for underfill applications.* Journal of Colloid and Interface Science, 2005. **292**(2): p. 436-444.

35. A.D. Roberts, *Natural Rubber Science and Technology*. 1990, Oxford, UK: Oxford University.

36. L. N. Bacigalupo, Fracture Behavior of Nano-Scale Rubber-Modified Epoxies, in Polymer Science and Engineering. 2013, Lehigh University: Bethlehem, PA, USA.

37. Y. Huang and A. J. Kinloch, *Modelling of the toughening mechanisms in rubber-modified epoxy polymers.* journal of Materials Science, 1992. **27**(10): p. 2753-2762.

38. H.R. Azimi, R.A. Pearson, and R.W. Hertzberg, *Fatigue of hybrid epoxy composites: Epoxies containing rubber and hollow glass spheres.* Polymer Engineering & Science, 1996. **36**(18): p. 2352-2365.

Output (Acknowledge the Thailand Research Fund)

1. P. Dittanet*, R. A. Pearson, P. Kongkachuichay, *Thermo-Mechanical Behavior and Moisture Adsorption of Silica Nanoparticles Reinforment in Epoxy Resins*, International Journal of Adhesion and Adhesives, 2016 (submitted)
2. K. Leelachai, P. Kongkachuichay, P. Dittanet*, *Enhanced Toughness of Epoxy Composites Using Hybrid Silica Nanoparticles and Epoxidized Natural Rubber Fillers*, Polymer Testing, 2016 (submitted)

Applications

1. K. Leelachai, P. Kongkachuichay, P. Dittanet*, *Thermal and Mechanical Properties of Epoxy/Silica Nanoparticles/Epoxidized Natural Rubber Hybrid Nanocomposites*, The 5th TIChE International conference 2015 (Oral presentation)
2. P. Dittanet*, R. A. Pearson, P. Kongkachuichay, K. Leelachai, *Thermal and Mechanical Behaviors of Silica Nanoparticles Dispersed in Selected Epoxy Resins*, The 5th TIChE International conference 2015 (Poster presentation)