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Nanoparticle-modified epoxies Effect of test rate

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Abstract

This study compares the effect on the fracture energy of an epoxy polymer from the addition of different weight Silica and core-shell rubber (CSR) particles, and the hybrid of both (from 0.5 weight The fracture energies measured with TDCB specimens will also be compared with simulation results using the finite element analysis software Abaqus. The toughening mechanisms involved will be confirmed by fracture surface images obtained from field emission gun scanning electron microscopy (FEG-SEM).

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Chapter 1

1.1 Introduction

Epoxy is a thermoset polymer, which is highly crosslinked and brittle; hence there is a need to toughen epoxy for use in engineering applications. This project uses silica nanoparticles, core-shell rubber (CSR) particles and hybrids of both particle types, to investigate the toughening effect of epoxy with different weight % of nanoparticles at both quasi-static and high test rates. In addition, the work will investigate the synergistic toughening effects of combining silica nanoparticles with micron-sized rubber particles. There are two aspects in the effect of test rate study: the effect of different weight % of nanoparticles added, and the effect of different test rate (i.e. quasi-static and high rate). Silica particles will be added in at concentrations of 0.5, 1, 2, 3, 5, 10, 15 and 20 weight %, and at the maximum possible concentration (25.4 weight %). CSR particles will be added in at the same weight percentages, but up to a maximum of 10 weight %. In previous work [1–3], the effects of different weight % of silica have been investigated with relatively large weight percentages of nanoparticles (of 10 weight % and above, e.g. from Hsieh et al. [2] and Mohammed et al. [4]) but not with small weight percentages. It has been suggested that small percentages of silica nanoparticles are more effective at toughening epoxy than large weight percentages, but this has not yet been investigated. Hence this study will provide more information about the effect of small percentages of silica. This effect can be shown and explained by comparing the fracture energy, G_c , against the weight % of silica nanoparticles. The toughening mechanisms have been identified as shear yielding in the epoxy plus debonding of the particles followed by void growth of the epoxy. The results would be expected to show a positive increase in toughness as the percentage of nanoparticles increases, and a plateau at the maximum point. However, only about 15% of the silica nanoparticles have been observed to debond [2]. The small weight % of SiO_2 particles added in could have a greater effect on the overall curve, as a higher % of the silica particles may be able to undergo debonding and void growth than at high % of silica particles, and hence

a steeper increase in G_c vs wt% than observed in the literature, such as from Hsieh et al. [2], at small weight% may be expected. For the effect of test rate, this study will start with a quasi-static rate, and then investigate the high rate effect. The higher test rate is expected to produce an increase in brittleness, and hence a reduction in the fracture energy. The hard silica particles are expected to show less of a reduction of toughness with increasing test rate when compared to the soft rubber particles. A fracture mechanics approach will be used to characterise the toughness of the epoxy.

Chapter 2

Literature review

2.1 Introduction

There is a long history in the use of adhesives in industry. There are many advantages in using adhesives in industry; one big advantage is the reduction of cost. There is also an improvement in product appearance, and an improvement in stress distribution and corrosion resistance, these factors enhance the design possibilities [5]. However, there are also drawbacks, for example adhesive bonding requires surface pretreatment of the substrates, it cannot join thick metallic components effectively, non-destructive testing methods are not applicable and it lowers the upper-service temperature [5]. In order to minimize these drawbacks, investigations into adhesive properties have been ongoing. To help the understanding and assessment of adhesive joints, finite element analysis (FEA) and fracture mechanics approaches are often used. These approaches can be used to predict service life and improve joint properties under different environments [5]. Due to the brittleness of adhesives, they are often modified by particles to improve their fracture toughness without changing their glass transition temperature, T_g [6]. However, some of the toughening mechanisms particle bridging, crack pinning and deflection are not applicable for nanoscale particles, as the particles are smaller than the crack opening displacement [6, 7]. Therefore the size of the particles used is one of the most important parameters in toughening epoxy. There is a higher critical stress for debonding for smaller particles, hence a reduced the amount of debonding would be expected. These toughening mechanisms can be investigated by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) and transmission optical microscopy (TOM) [6] can be used to assess the dispersion of the particles. Agglomeration of the particles can reduce the toughness of the polymer, and will increase the viscosity of the uncured resin which may lead to processing difficulties. There can be a large increase in toughness of the modified epoxy due to the toughening mechanisms described below, and the

increased toughness is also maintained when the epoxy is used in fibre composites [3]. The toughness of the modified epoxy depends on the amount of crosslinking of the epoxy, the type of particles used, the particles size and their concentration [3].

2.1.1 Rubber-toughened epoxy

There has been a long history in the use of rubber particles in the toughening of epoxy. It is established that the larger the rubber particles, the higher the stress concentrations [8] and hence a higher amount of localised deformation. There are two principal types of rubber-toughened epoxy: carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber and core-shell rubber (CSR) particles are commonly used. Carboxyl-terminated butadiene-acrylonitrile (CTBN) rubbers are rubbers containing butadiene and acrylonitrile as copolymers [9, 10]. They are added as a liquid rubber which dissolves in the epoxy resin and phase-separates to form particles during curing of the epoxy. Examples of different extents are amino-terminated-acrylonitrile (ATBN) and vinyl-terminated butadiene-acrylonitrile (VTBN). The use of block copolymers can also provide a different microstructure of phases (for example spherical micelles, vesicles and worm-like micelles) and hence can enhance toughening [11, 12]. There are two requirements for the CTBN rubber to be added to the epoxy: 1. the rubber must be able to dissolve in the epoxy first and then able to precipitate out during curing, and 2. the rubber must be able to react with the epoxide group to ensure good interfacial bonding between the particle and the epoxy. The particle size or diameter, d , of the CTBN rubber particles depends on the curing cycle, volume fraction, V_p , and concentration of the butadiene and acrylonitrile in the rubber. Larger rubber particles would be formed when a slow curing process is used. When the amount of rubber added increases, their diameter and volume fraction would increase too [13-15]. At high concentrations phase inversion can occur, where the rubber can become the matrix with epoxy particles inside [16]. The rubber would stay in a dispersed phase when its concentration is less than 20 wt%. Core-shell rubber (CSR) particles are pre-formed rubber particles with a soft core and a hard outer shell. The glassy polymeric shell can prevent the rubber particle aggregating and deforming during processing [11]. The CSR structure can be designed according to different factors (such as the chemical components of the matrix). Multilayer structures are very commonly used [10]. The particles are preformed, so the diameter is not dependent on the curing process, unlike CTBN. The major toughening mechanisms for rubber particles are localized plastic shear yielding and particle cavitation [11], followed by plastic void growth, these are discussed in Section 2.5. The toughening mechanism

in rubber toughening is due to the change in yield shear stress at the crack tip, which reduces the stress concentration of the region and enhances optimal shear banding. In order for this mechanism to occur, the stress fields near particles need to be overlapped and the spaces between them are critical [18].

2.1.2 Silica-toughened epoxy

It has been established that the addition of silica (SiO_2) nanoparticles can increase the toughness of epoxy [1, 7]. A sol-gel process is used to produce these silica nanoparticles (SiO_2), as liquid sol is transformed into a solid gel phase. The increase in the When adhesion is low at the interfaces between the silica particles and the epoxy, there would be more debonding of particles, and leads to more plastic void growth [7, 19, 21]. Shear banding and void growth are the major toughening mechanisms in silica nanoparticle-modified epoxy [6]. The toughening mechanisms in silica-modified epoxy is similar to other particles, but there is no crack pinning [1, 19], discussed in Section 2.5, because the particle diameter is less than the crack-opening displacement. Work on silica nanoparticle-modified epoxy performed by Hsieh et al. [19] has shown that some of the common fracture mechanisms (crack pinning, crack deflection and immobilised polymer around particles) can be discounted for silica nanoparticles. The major mechanism there was plastic deformation of epoxy. This means that the particles debonded from matrix, there were highly localised stress concentrated regions, which caused plastic deformation of the epoxy. There have also been studies of addition of both rubber and silica particles and they show good toughening effect [22]. It is because these two types of particles provide a good balance of modulus and toughness [23]. A synergy effect was found, giving a significant increase in toughness, from studies by Hsieh et al. [24] and Manjunatha et al. [23], with the use of a combination of silica and CTBN particles. With the use of block copolymers or CSR with silica particles, synergy effect in terms of toughness was also found to increase in the study from Chen et al. [25, 26].

2.1.3 Fracture mechanics

There are different theories in the study of fracture mechanics, the two main approaches to quantify toughness are by the consideration of the energy approach and stress intensity approach [17]. Linear elastic fracture mechanics (LEFM) is used in considering the fracture circumstances in epoxy polymers indicate a linear elastic response with plasticity confined to only a small zone at the crack tip. At the crack tip, there are different directions of stresses; therefore, there would be different modes of loading. All

the three modes of loading (mode I, mode II and mode III) would occur at the crack tip, see Figure 1, all of them are considered [17], but mode I is the most critical one as it has the lowest energy and hence the most likely to cause fracture.

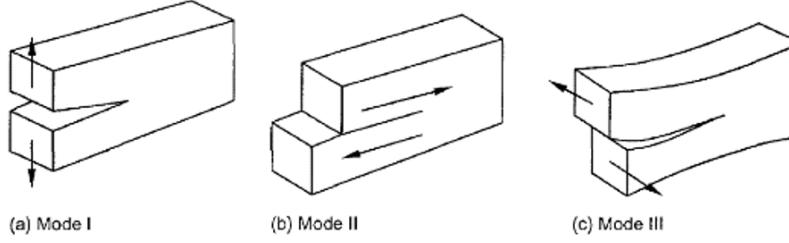


Figure 2.1: The different modes of loading [27]

2.1.4 Fracture toughness

There are two approaches to calculate fracture toughness, one is based on energy while the other considers the stress intensity of the crack. 1) Energy approach: fracture occurs when sufficient energy is released from the stress field by growth of the crack. The energy criterion [28] is:

$$-\frac{1}{B} \frac{dU}{da} \geq G_C \quad (2.1)$$

where B = width of crack front, U = potential energy of the loaded specimen, a = crack length and G_c = fracture energy (critical strain energy release rate). For bulk linear elastic behaviour away from the crack tip, G_c is given by:

$$G_c = \frac{P_c^2}{2B} \frac{dC}{da} \quad (2.2)$$

where P_c = load required for fracture (crack propagation), and C = compliance (displacement/load) of the specimen. 2) Stress intensity factor approach: The critical stress parameter is the critical stress intensity factor, K_C , which is expressed in a slightly different way under plane stress and plane strain [17]. To be conservative, the minimum value is desired, so plane strain conditions are considered in tests. For plane stress (i.e. a thin sheet):

$$K_c^2 = E G^c \quad (2.3)$$

$$K_c^2 = \frac{E}{1 - \nu^2} G_c^c \quad (2.4)$$

where E = Young's modulus and ν = Poisson's ratio [17]. The correlation between G_c and K_c in plane strain is [29, 30]:

$$G_c = \frac{(1 - \nu^2) K_c^2}{E} \quad (2.5)$$

The plane stress and plane strain conditions also have an effect on the plastic zone at the crack tip; the radius of the plastic zone at the crack tip, r_y , see Figure 2, can be expressed as [29]: For plane stress (i.e. a thin sheet):

$$r_y = \frac{1}{2H} (K_c / \sigma_Y) \frac{dC}{da} \quad (2.6)$$

For plane strain (i.e. a thick sheet):

$$r_y = \frac{1}{6H} (K_c / \sigma_Y) \quad (2.7)$$

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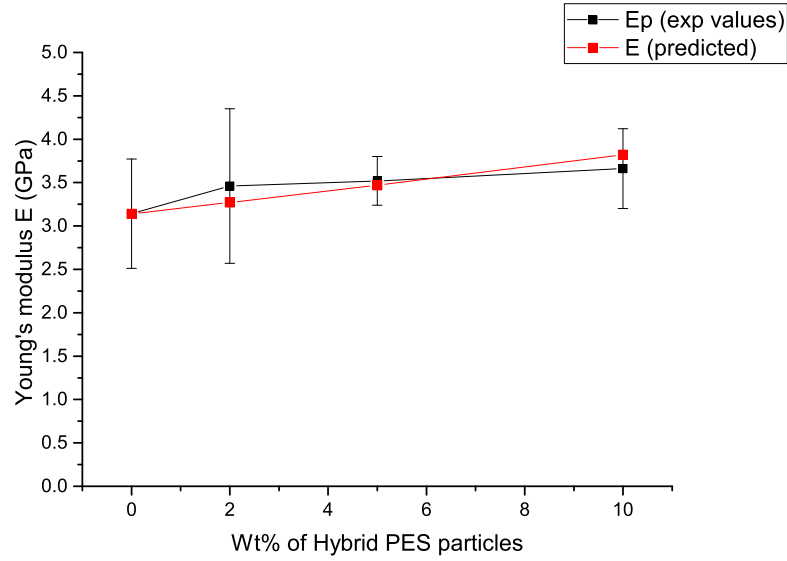


Figure 2.2: A Figure

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2.1.5 My Subsection 1

Just refer to Table 2.1

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Table 2.1: My Table Caption

2.1.6 My Subsection 2

Now there are two ways to type equation one is $e = mc^2$ or $e = mc^2$ The other see Eq. (2.8). This is the reference [?]

$$\frac{Numerator}{Denominator}(\sigma) \tag{2.8}$$

2.2 Second section

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Chapter 3

Second Chapter

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Bibliography

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Appendix A

Appendices

This is the appendix