FATIGUE RESISTANCE OF TOUGHENED EPOXY RESINS MODIFIED WITH PREFORMED POLYMER PARTICLES

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Abstract

Fatigue resistance of toughened epoxy resins with preformed polymer particles were studied in terms of the fatigue threshold and the fatigue crack propagation (FCP). The toughening modifiers were polyamide-12 (PA12) and core-shell rubber (CSR). The PA12 toughened epoxy achieved higher stress intensity factor range (ΔK) than the pure epoxy, irrespective of the molecular weight between cross-links (Mc) of the epoxy matrices. The crack bridging of the PA12 particles was the major mechanism of the fatigue resistance. Meanwhile, the fatigue behavior of the CSR / epoxy resins depended on the Mc. The whole FCP curve of the CSR / epoxy with low Mc was in the high ΔK. However, the fatigue threshold of the CSR / epoxy with high Mc was in the lower ΔK than that of the pure epoxy. The plastic deformation of the epoxy matrix with high Mc was localized, which decreased the fatigue resistance.

1. Introduction

Epoxy resins have been widely applied as matrix resins of fiber reinforced composites and structural adhesives. Fatigue properties are very important for long-term reliability of the materials in the structural applications. Various types of toughening technologies have been studied to improve the resistance to the crack propagation in the epoxy resins. Rubber toughening is well-known technology which has been studied by many researchers [1-5]. The toughening mechanism usually involves enhanced localized shear yielding of the epoxy matrix resins in front of the crack tip. The mechanism depends on the deformation of the epoxy matrix, so that the toughening effect of the rubber decreases as the crosslink density of the epoxy matrix becomes greater. Therefore, the rubber toughening tends to compromise high temperature performances of the epoxy matrices. The promising toughening approach with keeping the high temperature performances of the resins is addition of preformed thermoplastic polymer particles [6-8]. The toughening mechanism was particle-bridging behind the crack tip. In other words, the toughening effect relies on the particles themselves and the interfacial adhesion between the particles and the matrix resins. However, the fatigue resistance of these toughened epoxy resins using the polymer particles has not been clarified yet. The objective of this study is to investigate the fatigue resistance of the toughened epoxy resins with the preformed polyamide-12 (PA12) particles and the toughened epoxy resins with core-shell rubber (CSR) particles. The fatigue resistance and the mechanisms were studied in terms of the fatigue threshold and the fatigue crack propagation (FCP).

2. Experimental

2.1. Materials and Sample preparation

The materials used in this study were three types of diglycidyl ethers of bisphenol A (DGEBA) epoxy resins with different weight per epoxy equivalent (Epikote 828, 1001, 1004 ; manufactured by Mitsubishi Chemical). Ep828 is a liquid type epoxy resin with an average molecular weight of 370g/mol. Ep1001 and Ep1004 are solid type epoxy resins with an average molecular weight of 900g/mol and 1650g/mol, respectively. The epoxies were mixed and stirred in oil bath to make several types of the base resins with different molecular weight between cross-links (Mc). These resins were blended with toughening modifiers. Two kinds of pre-formed polymer particles were utilized as the toughening modifiers: polyamide-12 (PA12) particles and core-shell rubber (CSR) particles. Preformed PA12 spherical particles with 6µm average diameter (SP500 manufactured by Toray Industries, Inc.) were used because of the high toughness and good adhesion with epoxy resins. The CSR particles used here were manufactured by Kaneka Corporation, Japan. The CSR particle consists of the core of poly (n-butyl acrylate) and the shell of poly (methyl methacrylate) having functionality to react with epoxy resins. The particle size was about 0.1µm. The epoxies were cured with stoichiometric amounts of 4, 4’-diamino diphenyl sulphone (DDS). The curing condition was 150^{o}C for 3h, and followed by 2h-postcure at 180^{o}C.

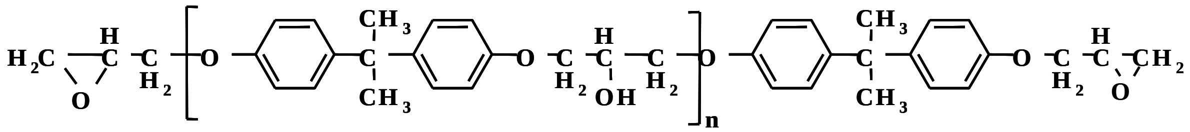


Figure 1. Chemical structure of epoxy resin (DGEBA).

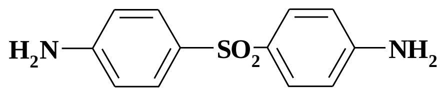


Figure 2. Chemical structure of curing agent (DDS).

2.2. Evaluation methods

The temperature dependencies of the viscoelastic properties (storage modulus: E’) of the cured epoxy resins were evaluated by dynamic mechanical analysis (DMA) method in the bending mode using a dynamic frequency of 1Hz. The molecular weight between cross-links (Mc) of the cured resins was calculated from the theory of rubber elasticity using the following equation (1),

$$M_c = \frac{3\phi\rho RT}{E_r} \quad (1)$$

where φ is front factor (= 1.3), ρ is the density of the cured epoxy resin, R is gas constant, T is the temperature of the Tg (peak temperature of tanδ) + 40 ^oC of the cured epoxy resin, and E_r is the storage modulus in the rubbery plateau at the temperature (Tg + 40 ^oC) obtained from the DMA.

Compact tension (CT) specimens were machined from the cured plates to determine the fracture toughness and the resistance in the fatigue crack propagation (FCP). The configuration of the CT specimen is shown in Figure 3 according to ASTM D 5045. Width, W, was 32.5mm, thickness, B, was 6mm and initial crack length, a, was 13-15mm. Pre-crack was introduced with a blade by impact. Strain gauges were mounted on the back face of the specimen to control the fatigue test.

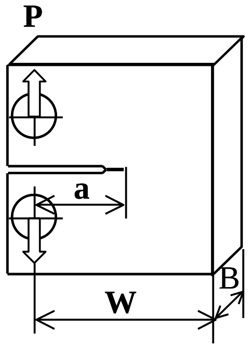


Figure 3. Configuration of compact tension (CT) specimen.

Fracture toughness was evaluated using a servo-hydraulic testing machine (Shimadzu, servopulser EHF-FD05, capacity 4.9kN) at a tensile rate of 1mm/min. The fracture toughness, K_{Ic} was calculated using the following equation (2), from applied load, P, crack length, a, width, W, and thickness, B.

$$K = \frac{P}{BW^{1/2}} \frac{\left(2+\frac{a}{W}\right)\left(0.886+4.64\frac{a}{W}-13.32\left(\frac{a}{W}\right)^2+14.72\left(\frac{a}{W}\right)^3-5.6\left(\frac{a}{W}\right)^4\right)}{\left(1-\frac{a}{W}\right)^{3/2}} \quad (2)$$

The fatigue crack propagation (FCP) resistance was evaluated in the same system at a frequency of 5 Hz with a load ratio of 0.1(minimum load / maximum load). Stress intensity range ΔK, was calculated from maximum and minimum stress intensity factors, $K_{\max}$ and $K_{\min}$, corresponding to the maximum and minimum load, respectively. The crack propagation rate, *da/dN*, was obtained from the crack length measured during test.

The fracture surfaces and the cross sections after the tests were observed with electron microscopes (TEM, SEM) and an optical microscope (OM).

3. Results and Discussion

Fatigue crack propagation (FCP) behaviors of toughened epoxy resins (Mc=1440g/mol, 3060g/mol) with PA12 particles were shown in Figure 4. The FCP curves of the PA12 toughened epoxy resins shifted to higher stress intensity factor range (ΔK) than those of pure epoxy resins. For the matrix resin with Mc=1440g/mol, the threshold ΔK of the pure epoxy was 0.3MPa $m^{1/2}$. The threshold ΔK of toughened epoxy with the 10wt% PA12 was 0.4MPa $m^{1/2}$, which was 33% higher than that of the pure epoxy. For the matrix resin with Mc=3060g/mol, the threshold ΔK of the pure epoxy was 0.4MPa $m^{1/2}$. The threshold ΔK of toughened epoxy with the 10wt% PA12 was 0.5MPa $m^{1/2}$, which was 25% higher than that of the pure epoxy.

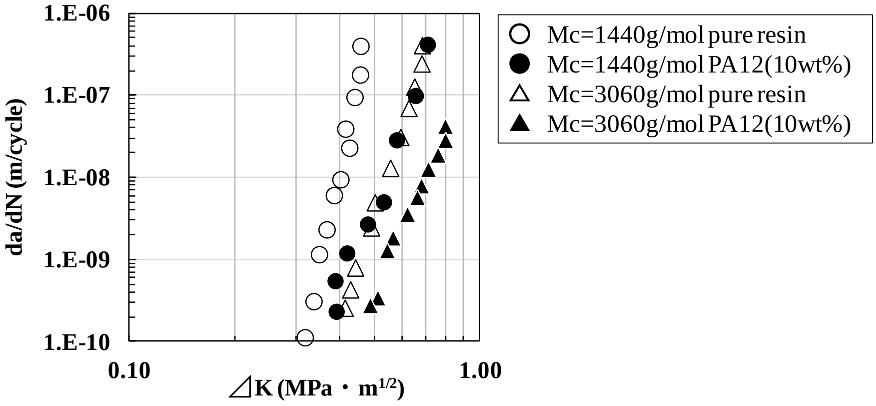
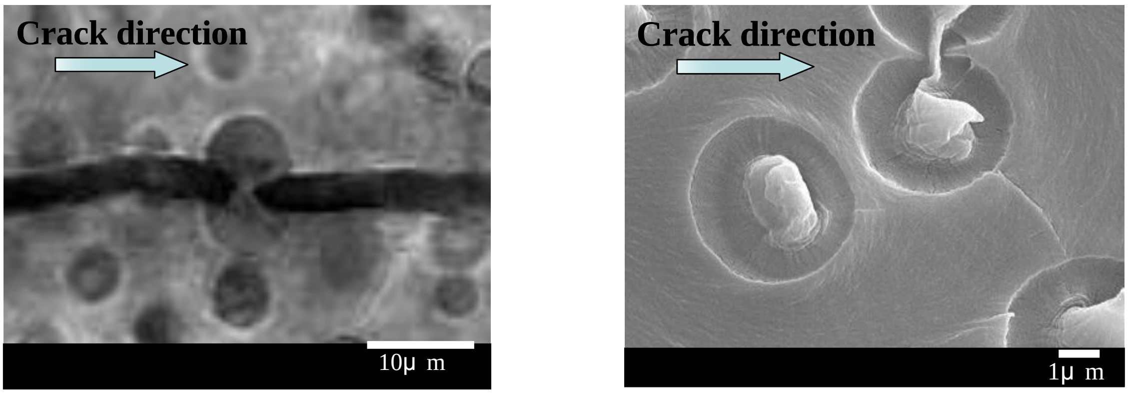


Figure 4. FCP curves of toughened epoxy resins with PA12 particles.

Figure 5 shows OM (a: cross section) and SEM (b: fracture surface) images of the toughened epoxy resin with PA12 particles. The particle-bridging of PA12 can be seen in both images, which is the main mechanism to give the fatigue resistance. These results indicate that both the mechanical properties (the modulus of elasticity, the plastic deformation capacity, and the toughness) of the PA12 particles and the interfacial adhesion (PA12 particles / epoxy matrix) were the dominant requirement to achieve the fatigue resistance of PA12-toughened epoxy.



a) cross-section around fatigue crack

b) fracture surface

Figure 5. Cross section and fracture surface of toughened epoxy resin with 10wt% PA12 particles.

Meanwhile, the FCP curves of toughened epoxy resin with 5wt% CSR particles were shown in Figure 6. The fatigue behavior was different from the toughened epoxy with PA12 particles, especially in terms of the effect of the Mc of the epoxy matrix resins. For the higher cross-linked epoxy resin (Mc = 1440g/mol), the whole FCP curve of the CSR / epoxy was in the higher ΔK than that of the corresponding pure epoxy matrix. However, the FCP curve of CSR / lower cross-linked epoxy (Mc = 3060g/mol) intersected the FCP curve of the pure epoxy matrix. Namely, the FCP curve of the CSR / epoxy showed higher ΔK in the fast fracture (high da/dN) region, but the threshold of the CSR / epoxy was in the lower ΔK than the threshold of the pure epoxy. The fatigue resistance of the lower cross-linked epoxy (Mc = 3060g/mol) decreased by the CSR addition.

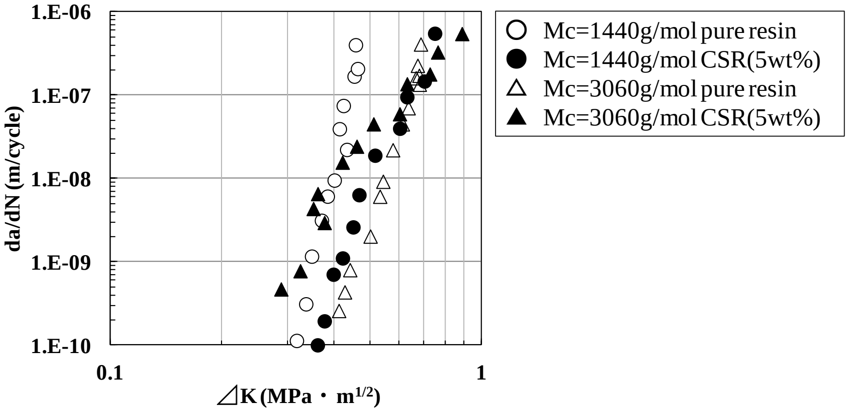


Figure 6. FCP curves of epoxy resins modified with CSR particles.

In order to elucidate the dominant factors to determine the fatigue resistance, the deformation behaviors of these resins with different cross-link densities were examined. Figure 7 shows SEM photographs of the fracture surfaces of the two CSR modified epoxy resins. The behaviors on deformation and fracture at fatigue threshold depended on the Mc of the epoxy matrix resins. In case of higher cross-linked epoxy (Mc = 1440 g/mol), small cavities were observed (Fig.7 a & c), which were originated from the cavitation of the CSR particles. The plastic deformation of the epoxy matrix surrounding the cavities was not clear on the fracture surfaces. Meanwhile, in case of the lower cross-linked epoxy (Mc = 3060 g/mol), the plastic deformation surrounding the large cavities in the epoxy matrix was clearly observed on the fracture surfaces (Fig.7 b & d).

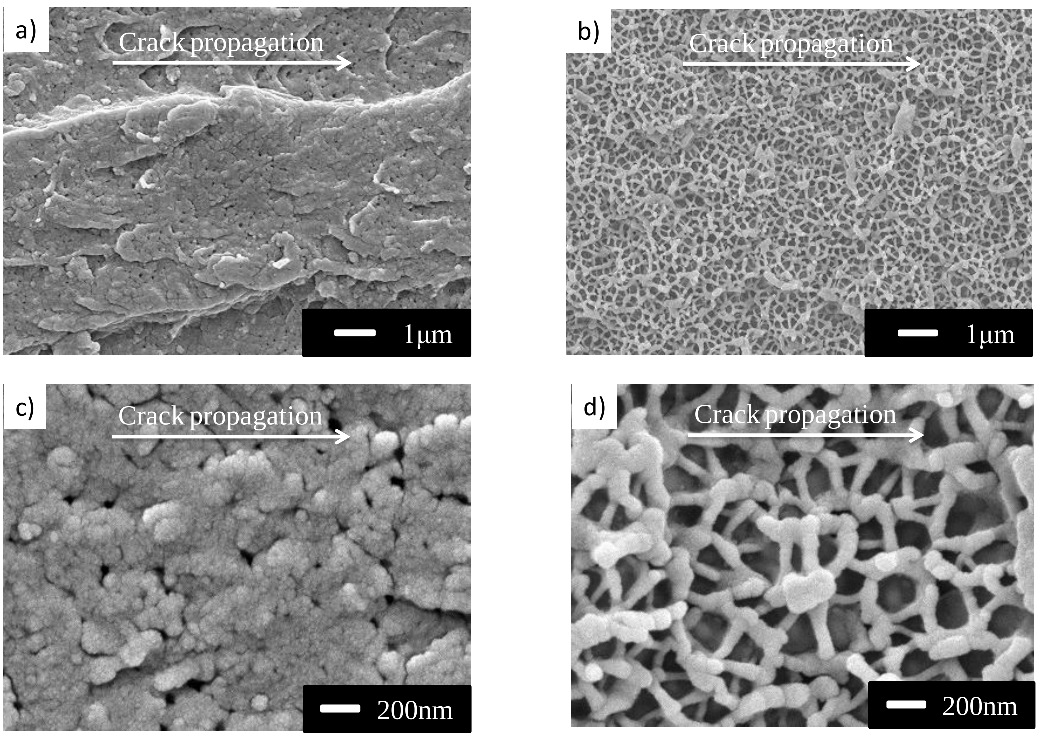


Figure 7. SEM images of the fractured surfaces of toughened epoxy resins with 5wt% CSR particles at fatigue threshold: (a) and (c) Mc = 1440 g/mol., (b) and (d) Mc = 3060 g/mol.

From the observed plastic deformation on the fracture surfaces, it might be estimated that the low cross-linked epoxy could absorb more energy and the FCP should be in the higher ΔK region than that of the highly cross-linked epoxy. However, the fact was different from the estimation. Namely, the fatigue threshold of the low cross-linked epoxy with the CSR was lower than that of the high cross-linked epoxy with the CSR.

The cross-sectional images around the crack tip (Figure 8) clarified the reason. In the highly cross-linked epoxy (Mc = 1440 g/mol), shear bands (plastic deformation) diffused toward several directions around the crack tip, with the cavitation of the many CSR particles in the epoxy matrix. The diffused shear bands could absorb much energy, which suppressed the FCP. On the other hand, in the low cross-linked epoxy (Mc = 3060 g/mol), the cavitation of the CSR and the shear bands of the epoxy matrix were localized mainly in the direction ahead of the crack tip. The localization of the plastic deformation in the limited area, which could absorb only small energy, did not prevent the FCP at the low K.

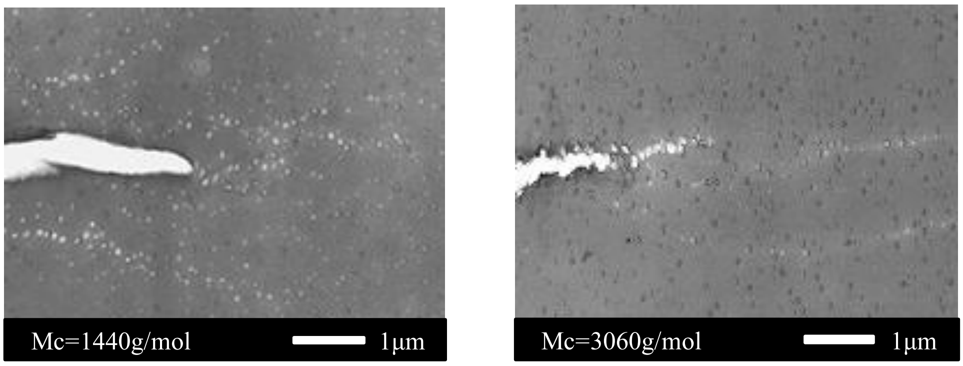


Figure 8. TEM images of the epoxy resins modified with 5wt% CSR at fatigue threshold.

The CSR particles in both epoxy resins are the same. Namely, the required stress condition to cavitate the CSR particles are the same. Then, why many CSR particles were cavitated in the highly cross-linked epoxy matrix, and why the cavitation of the CSR particles in the low cross-linked epoxy was limited? The actual stress states around the crack tip in these CSR modified epoxy matrices would be different each other. It is estimated that the required stress condition for the cavitation could be achieved in wide area in the highly cross-linked epoxy with 5wt% CSR, but the same condition could not be achieved in the low cross-linked epoxy.

The stress state in the epoxy matrices should also depend on the concentration of the CSR particles in the epoxy matrices. Figure 9 shows the FCP curves of the low cross-linked epoxy (Mc = 3060 g/mol) with several amount of the CSR particles. Figure 10(a) picked up the fatigue threshold in relation to the concentration of the CSR. The fatigue threshold of the CSR / low cross-linked epoxy began to decrease compared to that of the epoxy matrix when the amount of the CSR exceeded 0.1 wt%. These results can be rewritten in relation to inter-particle distance, as shown in Figure 10(b). When the inter-particle distance becomes shorter than 0.8μm, the fatigue threshold of the CSR modified epoxy resin began to decrease.

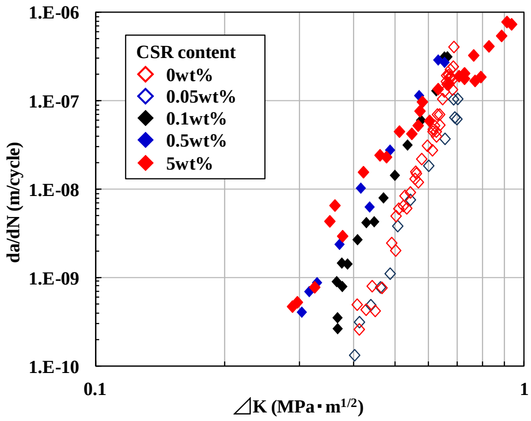


Figure 9. FCP curves of the low cross-linked epoxy (Mc = 3060 g/mol) with several amount of CSR particles.

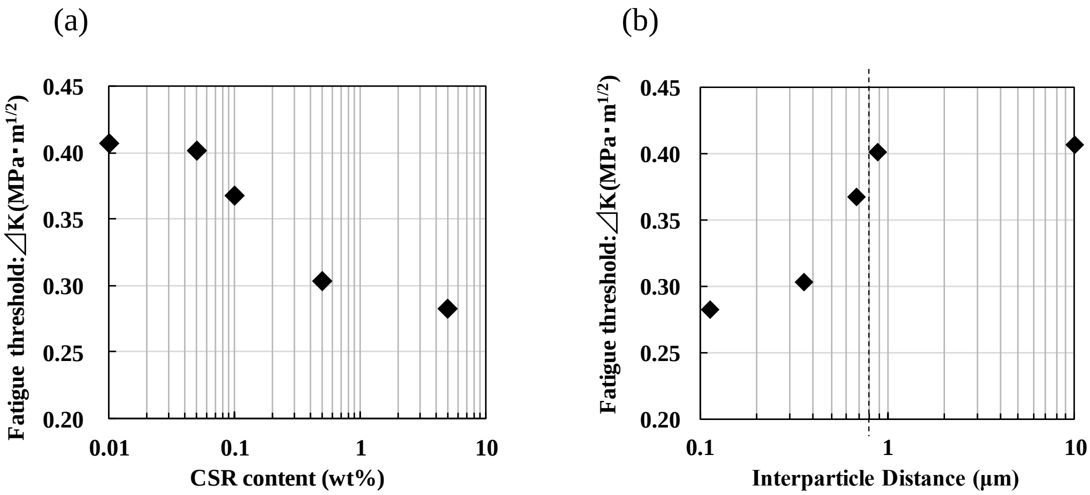


Figure 10. Fatigue threshold of the low cross-linked epoxy (Mc = 3060 g/mol) with CSR: the relationship with (a) CSR content, (b) inter-particle distance.

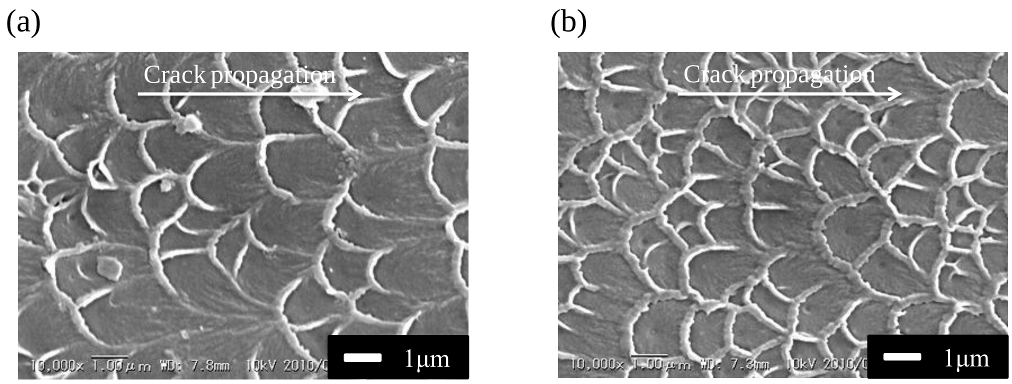


Figure 11. SEM images of the fractured surfaces of toughened epoxy resins (Mc = 3060 g/mol.) with different amount of CSR at fatigue threshold: (a) 0.05wt% CSR, (b) 0.1wt% CSR.

Figure 11 shows the fracture surfaces of the CSR / low cross-linked epoxy resins at the fatigue threshold. The large plastic deformation (white lines) of the epoxy matrix between the cavitated CSR particles began to connect each other when the amount of the CSR exceeded 0.1 wt%. The concentration of the CSR was coincident to the amount where the decrease of the fatigue threshold began. The "ligaments" among the cavitated particles could easily yield and break. Namely, the capacity of the load bearing of the local area would be very small. It is assumed that the continuation of the plastic deformation of the epoxy matrix (continuous yielding among cavitated CSR particles) in the local area ahead the crack tip would be the key factor to determine the fatigue threshold of the CSR / epoxy blends.

4. Conclusions

Fatigue resistance of toughened epoxy resins with preformed polymer particles were studied in terms of the fatigue threshold and the fatigue crack propagation (FCP). The PA12 toughened epoxy achieved higher stress intensity factor range (ΔK) than the pure epoxy, irrespective of the molecular weight between cross-links (Mc) of the epoxy matrices. The crack bridging of the PA12 particles was the major mechanism of the fatigue resistance. Meanwhile, the fatigue of the CSR toughened epoxy resins depended on the Mc of the epoxy matrices. The whole FCP curve of the CSR / epoxy with low Mc (high cross-link density) was in the high ΔK. However, the fatigue threshold of the CSR / epoxy with high Mc (low cross-link density) was in the lower ΔK than that of the pure epoxy. The plastic deformation of the epoxy matrix with high Mc (low cross-link density) was localized mainly in the direction ahead the crack tip, which decreased the fatigue resistance. The fatigue resistance (especially the fatigue threshold) of CSR / epoxy depends much on the deformation behaviors of the epoxy matrix and the inter-particle distance between the CSR particles.

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