論 文 の 要 旨

題　目　A Study on The Dynamic Compressive Behaviors of Epoxy Adhesive Modified by Mixed Silica Micro-nanoparticles
（ミクロおよびナノサイズのシリカフィラーを充填したエポキシ接着剤の動特性に関する研究）

氏　名　Yohanes

The structural adhesives ability to join various type of materials, very thin materials, dissimilar materials, and lightweight composite materials is crucial to reduce the weight of the structures. Currently, the use of the adhesives in lightweight structures, such as in automobile and aircraft, is increasing. Among those adhesives, epoxy is commonly used owing to its strong adhesion and high compatibility with the various type of materials. In the applications, the joints are subjected by dynamic loadings, such as impacts and vibrations, at a wide range of temperature. Therefore, the present study focusses on knowing the stiffness and damping behaviors of the epoxy adhesive under impact loadings which are crucial to the design and analysis of the structures.

Chapter 1 introduces the topic and the objectives of the present study. This chapter also describes the progress of study on the mechanical behaviors of the neat epoxy adhesive and the epoxy modified by silica. The epoxy adhesives are viscoelastic by nature which are sensitive to both loading rate and temperature. The stiffness and damping behaviors of epoxy are characterized by their storage modulus and loss modulus, respectively. These properties are governed by their crosslink density during polymerization. Rigid silica particles are introduced as fillers to increase the stiffness by forming the interphase which is stiffer than the epoxy matrix. The key factor to effectively improve the stiffness is by creating large and continuous interphase in the epoxy/silica composite. In the previous studies, the stiffness and toughness of the epoxy modified by single size silica particles had been investigated extensively. Under the static loadings, the stiffness was increased by increasing the content and reducing the size of silica particles. Constitutive models are also developed to predict the stiffness and provide the mixture law. However, the stiffening effect of silica particles depends on the quality of particle distribution. Under dynamic loadings, the stiffness was increased by the increased of silica content and loading rate which restrict the deformation of the epoxy matrix. The epoxy was embrittled by the dynamic loadings, but it regained the ductility by the presence of silica nanoparticles. Those results indicate that introducing silica nanoparticles improved the damping of epoxy under dynamic loadings. However, without any treatment, silica nanoparticles tend to agglomerate which reduce the intensity of matrix-filler interactions and thus, reduce the positive effects. Then, combining nanoparticles with microparticles was introduced to prevent the agglomeration. The effects of silica micro-nanoparticles on the stiffness and the fracture energy of epoxy under static loadings had been investigated by only few researchers. They found that silica micro-nanoparticles were well-dispersed and generated a synergistic effect that improved the fracture energy, but negligibly affected the stiffness. However, to the best author knowledge, the effects of silica micro-nanoparticles on the stiffness and the damping of epoxy adhesive under dynamic loadings have not been investigated. Therefore, the main objective of the present study is to evaluate the effects of the content and composition ratio of silica micro-nanoparticles on the dynamic stiffness and the damping behaviors of epoxy adhesive under impact loadings.

The split Hopkinson pressure bar (SHPB) tests have been conducted to obtain the dynamic stress-strain responses of the epoxy adhesive. In chapter 2, the specimens are sandwiched between the pressure bars and heated at the varied temperature of 15, 40, and 50°C. The content and the composition ratio of silica micro-nanoparticles in the epoxy specimens are varied at 5 and 10% by weight (wt.%) and from 0% (pure microparticles) to 100% (pure nanoparticles), respectively. The stiffness is estimated from the initial slope of stress-strain responses. However, poor contact between the bars and the specimen during unloading prevents direct estimation of damping from the area of stress-strain responses. Therefore, another approach to estimate damping is introduced. Considering that the area covered by the strain pulses is related with the strain energy, then, the damping is estimated from the difference of the total strain energy calculated at the input bar with the strain energy calculated at the output bar. Using a similar approach, the stress transmissibility is also estimated from the area of the transmitted pulse. Both damping and stress transmissibility are normalized by the area of the incident pulse for a fair comparison between each test conditions. The results show that stiffness and damping are increased by the increased of silica content and varied nonmonotonically by the composition ratio of micro-nanoparticles. Combination of micro-nanoparticles exhibit lower stiffening effects but provide higher damping compared to pure micro or nanoparticles. Such contrast behaviors indicate a trade-off between the stiffness and damping which are induced by matrix-particles interactions. These interactions induce damages and local plastic deformations which facilitate more energy dissipation but reduce the load transfer between matrix and particles and thus, reduces both stiffness and stress transmissibility. Despite that trade-off, there is an optimum composition ratio of 25% (25% nanoparticle:75% microparticle) at silica content of 10-wt.% which maximizes the damping while preserving the remarkable stiffening effect. The effectiveness of silica particles to increase the stiffness of epoxy are reduced by the increase of temperature and negligibly small as the temperature approach the glass transition temperature of the epoxy (T_g=55°C). Remarkable stiffening effects, however, are still obtained at the temperature of 40°C.

Poor particle dispersion and poor contact of bar-specimen are responsible for low stiffening performances and large deviations on the damping estimation obtained in chapter 2, respectively. It is noticed that high viscosity of epoxy and mixing all components at a time reduce the effectiveness of mixed micro-nanoparticles to improve particle dispersion. Therefore, in the following study presented in chapter 3, the specimen preparation and the SHPB test method are modified to improve particle dispersion.

In chapter 3, instead of sandwiched, the specimen was bonded between the input bar and the output bar. This test modification is intended to maintain proper contact between bar-specimen during the test period and thus, to obtain reliable and accurate damping estimation. In the specimen preparation, the epoxy is pre-heated to reduce its viscosity and the micro, and nanoparticles are mixed sequentially to obtain better particle dispersion. The content and the composition ratio of silica micro-nanoparticles are varied at 2, 5, and 10-wt.% and from 0% (pure microparticles) to 100% (pure nanoparticles), respectively. Reliable stress-strain loops are obtained using the modified SHPB tests so that the damping is directly estimated from the loop area and the stiffness is estimated from the initial slope. The results demonstrate that at the silica content of 5-wt.% the combination of micro and nanoparticles work synergistically to provide higher stiffening effect and damping on the epoxy simultaneously compared to pure micro or nanoparticles. However, at a lower silica content of 2-wt.%, the stiffening effect is governed by the nanoparticle content rather than the combination of micro and nanoparticles. This result indicates that the nanoparticles are well-dispersed without the help of the microparticles. However, such well-dispersed low silica content restricts the matrix mobility and thus, reduce the energy dissipation through matrix deformation. At a higher silica content of 10-wt.%, the combination of micro and nanoparticles is less effective to improve particle dispersion and deteriorate the stiffness and the damping performances. Finally, the optimum composition ratio of 25% nanoparticles:75% microparticles at silica content of 5-wt.% synergistically increases the intensity of matrix-filler interactions and thus, maximize both stiffness and damping of epoxy by 45% and 40%, respectively. Better particle dispersion is responsible for such synergistic effects by creating larger interphase and inducing damages and local yielding. In fact, the occurrence of local yields and damages are indicated by the deflected stress-strain response from the linearly elastic line and the remaining strain deformation after test period, respectively. The disturbed dynamic equilibrium condition during unloading also proves the existence of damages.

In summary, as concluded in chapter 4, the present study has demonstrated the effectiveness of mixed silica micro-nanoparticles to modify the stiffness and damping of epoxy adhesive even at high temperature of 40°C. The mixture law provides a wide range of design options to modify the dynamic performances of epoxy adhesive to match the applications. The key result of the present study is the simultaneous improvements on both the stiffness and damping provided by mixed silica micro-nanoparticles. Both stiffness and damping are crucial to maintain the structural rigidity and reliability, as well as to reduce the noise and vibration. Furthermore, the results of this study suggest a simple and low-cost alternative technique to exploit the reinforcing effects of silica nanoparticles without any extra mixing process. However, the effectiveness of silica micro-nanoparticles to improve particles dispersion and produces such synergistic effects is limited by the viscosity of the epoxy matrix, the weight fraction of silica particles, and the mixing process. In the future, the effects of silica micro-nanoparticles on the adhesive joint performances under dynamic loadings are worth studying. Particles of high intrinsic damping are also worth combining with silica particles to improve the damping performance facilitated by the damping mechanism other than the matrix damages so that the longer service life can be expected.