REPAIR OF DETERIORATED CFRP USING SUPER CRITICAL CARBON DIOXIDE

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Abstract

Once-mechanically deteriorated carbon fiber reinforced composite (CFRP) was repaired using super-critical carbon dioxide (sc-CO_2). Acrylonitrile monomer was penetrated deep into the deteriorated part of the composite using sc-CO_2, then it was polymerized there. The extent of the repair was evaluated using X-ray diffraction. This process was environmentally friendly, and it was found to be quite effective for repairing the CFRP. In addition, the "X-ray Diffraction Method" is a powerful tool for detecting the stress transfer of CFRP under transverse load in situ and non-destructively.

1 Introduction

Carbon fiber reinforced composite (CFRP) has been designed for complying a variety of demands. Then high performance CFRPs are available with a whole range of properties, and they are used in applications varying from aerospace to electronics and sports equipments. Continuous carbon fibers are often introduced unidirectionally in the composite for reinforcements, which possesses high elastic modulus and strength longitudinally. However, pronounced anisotropy results in inferior interfibrillar strength, and transverse cracking of the composite. Thus for the unidirectional fiber reinforced composites, it is important to clarify the transverse reinforcement effect and stress transfer. It has received detailed analysis, because of its significance for the prediction of mechanical performance of the composite, by using photoelasticity, spectroscopic techniques, mechanical modeling, infinite elemental analyses.

In this study, unidirectional continuous carbon fiber reinforced epoxy resin composite was subjected to the repeated stress in the direction perpendicular to the fiber direction. These stresses were transferred to the incorporated fibers through the matrix, which was appeared as the shift of the equatorial X–ray diffraction peak of carbon fibers. By detecting the peak shift quantitatively, we could get information how much stress the incorporated fiber was subjected to. By using this novel technique, *that is*, "X-ray Diffraction Method", we evaluated the stress transfer *in situ* and non-destructively in terms of microscopic point of view [1,2].

Then, the once-mechanically deteriorated CFRP was repaired using super-critical carbon dioxide (sc-CO_2). Among many properties of sc-CO_2, nowadays, sc-CO_2 is expected as an environmentally friendly solvent. Some monomers were penetrated deep into the deteriorated part of the composite using sc-CO_2, then it was polymerized there. The extent of the repair was evaluated using X-ray diffraction.

2 Experimental

2.1 Sample Preparation

A liquid diglycidyl ether of bisphenol A type epoxy resin (Epikote 828; Shell Chemical Co.), methyl tetrahydrophthalic anhydride as a curing agent, and 1-methyl imidazole as an accelerator were chosen for the resin system because of low viscosity before curing and high mechanical performance after curing. High modulus carbon fibers (TORAYCA M40B) were used as the reinforcements. Carbon fibers were impregnated into degassed epoxy resin, followed by pultrusion, curing at 80 ℃, 6h, and 180 ℃, 12 h, and finally unidirectional CFRP was obtained.

2.2 X-ray Diffraction

Rectangular strip of CFRP was clamped and set on the X-ray goniometer. Stress $\sigma_{\circ}$ was subjected to the whole composite in the direction perpendicular to the fiber axis, where equatorial

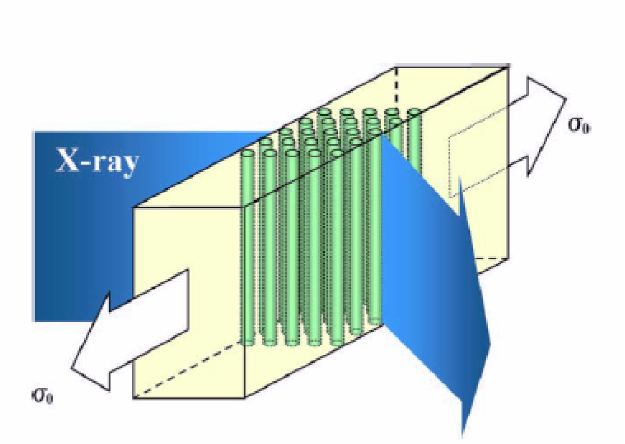

Fig. 1 Schematic model for the X-ray diffraction measurement.

reflection of carbon fiber can be detected as shown in Fig.1.

The stress σ_c on the incorporated fibers was evaluated by multiplying the crystal strain ε with the elastic modulus (36.5 GPa) of the intergraphite networks, which is perpendicular to the direction of covalent bonds.

3. Results and Discussion

Fig.2 shows the relationship between the stress σ_c on the incorporated CF crystal and the stress σ_0 applied on the whole composite. With increasing σ_0, the σ_c increased linearly in the initial stage. The initial slope can be correlated to the efficiency of the stress transfer to the incorporated fiber. Thus, this indicates that the stress was certainly transferred to the fiber through the matrix. Sudden breakage occurred around 14 MPa, which will be due to the interfacial failure between the matrix and the fibers. However, the remained fibers seem to be still stressed even after the macroscopic failure. This is quite important in the view point of damage tolerance for CFRP after undergoing the stress more than the tolerance limits. When the CFRP was subjected to the tensile stress of 10 MPa for 2000 times repeatedly in the direction perpendicular to the fiber axis, the initial slope decreased. This reveals that CFRP was mechanically deteriorated.

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Fig. 3 shows the relationship between the stress σ_c on the incorporated CF crystal and the stress σ_0 applied on as-prepared, deteriorated (by 2000 times cyclic stress of 10 MPa), deteriorated / repaired composites. Here, two kinds of repair were performed. One is that by impregnating acrylonitrile (AN) monomer to the mechanically deteriorated composite under sc-CO_2 condition, followed by polymerized *in situ.* The other is that by merely exposing the composite to AN monomer vapor, then

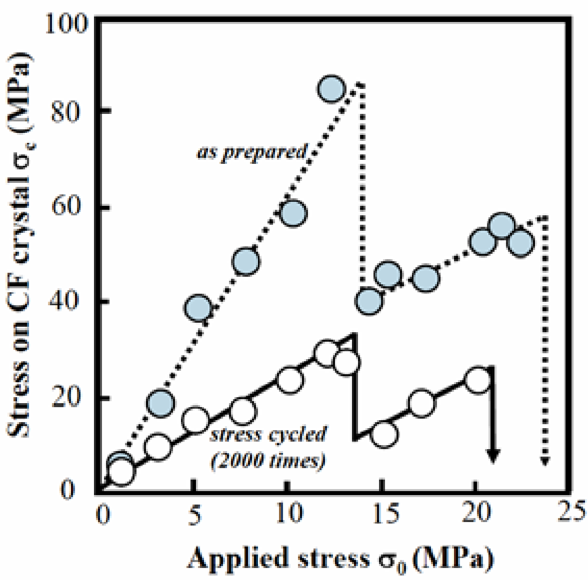

Fig.2 Relationship between the stress σ_c on the incorporated CF crystal and the stress σ_0 applied on the whole composite .

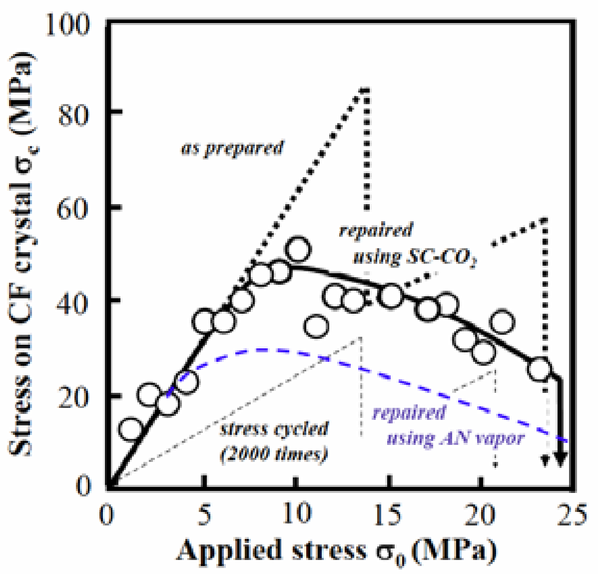

Fig.3 Relationship between the stress σ_c on the incorporated CF crystal and the stress σ_0 applied on the mechanically deteriorated / repaired composite . The results for as-prepared, deteriorated composites were also superimposed.

polymerized. It is clear that the stress transfer condition seems to be recovered to that of as-prepared sample up to 9 MPa of σ_o using SC-CO_2. On the contrary, by exposing the composite merely to AN vapor, the extent of the repair seems to be restricted to its initial stage. Accordingly, this process using sc-CO_2 is quite effective for repair the once deteriorated composite. In addition, the "X-ray Diffraction Method" is a powerful tool for detecting the stress transfer of CFRP under transverse load *in situ* and non-destructively.

4. Conclusions

"3R(recycle, reuse, reduce)" is a key word for the environmental issues. In addition to 3R, "Repairing" of the deteriorated materials is important, and it can be said to be the 4th "R" In this study, attention was paid to the repairing process using sc-CO2 (without using organic solvent) from the environmentally friendly point of view. This process was found to be quite effective for repairing the CFRP, judging from the stress transfer efficiency evaluated by X-ray diffraction.

References

[1] Nishino, T., Naito, H., Nakamura, K., Nakamae, K. "X-ray Diffraction Studies on the Stress Transfer of Transversely Loaded Carbon Fibre Reinforced Composite", *Composites*, Part A, vol.31 (11), 1225-1260 (2000).

[2] Nishino, T., Hirokane, D., Nakamae, K. "X-ray Diffraction Studies on the Environmental Deterioration of Transversely Loaded Carbon Fibre Reinforced Composite", *Composite Science and Technology*, vol.61, 2455-2459 (2001).