STUDY OF NOVEL CARBON FIBER COMPOSITE USED EXFOLIATED CARBON FIBERS

Masahiro Toyoda, Ryotaro Kohara, Tomoki Tsumura, Oita Univ., 700 Dannoharu, Oita, 870-1192 Japan
Hiroyuki Mutoh, Mototsugu Sakai, Toyohashi Univ. of Tech., Toyohashi 441-8580 Japan
Michio Inagaki, Aichi Inst. of Tech., Yakusa, Toyota 470-0392 Japan

Abstruct

On one of application for Carbon nano tubes (CNTs), its CNTs composite has been studied to reinforce of polymer. However, CNTs is not shown enough reinforced effect, because of poor dispersibility of CNTs and low purification. These problems are connected with the lowering mechanical strength in CNTs reinforced polymer composite. On the other hands, Exfoliated Carbon Fibers (ExCFs) prepared through electrochemical processing was found that it have unique morphology such as nano-meter sized fibril and mainly meso pores, and then have good despersibility. Fabrication of composite using its ExCFs was investigated. ExCFs changed in nanometer sized fibrils by ultrasonic treatment and CNTs were composited with Poly Methyl Meth Acrylate (PMMA) in-situ polymerization process, and them their mechanical properties were examined. Flexural strength and modulus of PMMA composite reinforced by ExCFs increased 166 % and 171 % comparison with bulk PMMA. In addition, it was better than that of PMMA composite reinforced by CNTs. ExCFs might be expected application to nano composite, in stead of CNTs.

Introduction

CNT have received much attention because of their interesting properties such as high modulus, and high electrical and thermal conductivity. Numerous researchers have been reported remarkable physical properties for the CNT. The CNTs in polymers hold a potential to improve the mechanical, thermal and electrical properties in the host material's one. Therefore, the CNTs have been expected to reinforce with polymer. Several methods to prepare the composite of them have been developed, e.g., solution casting, melt-mixing and in-situ polymerization of monomers with presence of the CNTs. Key issues for producing superior CNTs nanocomposites in this case are, widely recognized, (i) homogeneous dispersion of CNTs in polymeric matrix; (ii) strong interfacial interaction so as to effect load transfer from polymeric matrix to CNTs. Chen et.al., reported that addition of Multi Walled Carbon Nano Tubes (MWCNTs) reinforced polyurethane (PU) composite fibers have been fabricated by melt-extrusion. Significant improvement young modulus and tensile strength were achieved by imcorporating MWCNTs up to 9.3 wt% while without sacrificing PU elastmer's high elongation at break. Zhang et. al. reported effect of addition of 1 wt% CNTs into Poly amide resin (naylon-6) by simple melt compounding. Their effects resulted in 115%, 120% and 67% increase in tensile modulus, tensile strength and hardness, respectively. However, some problems such as contamination and homogeneous dispersion into matrix, has also been pointed out from many researcher. Its contamination is connected with the lowering of the strength in production of its composite used CNTs. Its reinforced effect of CNTs composite prepared is not perfect. On the other hands, ExCFs prepared by rapid heating through electrochemical processing in acid electrolyte was found to have unique morphology such as nano-meter sized fibril and meso pores by Toyoda et. al. Fabrication of composite using ExCFs was tried. Fibrous ExCFs nano-powders were mixed with monomer in-situ process. ExCFs composites with improved mechanical properties were fabricated by polymerization. The potential for nano-composites having extraordinary specific strength reinforced with ExCFs was discussed.

Exprerimental

The ExCFs were prepared by exfoliation of carbon fibers electrolyzed through electrochemical processing. Mesophase-pitch-based carbon fibers, having corrugate radial texture in their cross-sections and heat-treated at 2800 ^{o}C were used in the present study. Sizing agent on the surface of these carbon fibers was removed by washing in acetone. The carbon fibers were anodically polarized in HNO_3 electrolyte solution at a constant current 0.5 A by using a potentiostat/galvanostat. Preparation of graphite oxide throught electrolysis in HNO_3 electrolyte with 13 mol/dm^3 was carried out. The counter and reference electrodes were platinum and Ag/AgCl electrode, respectively. Carbon fibers after electrolysis were rinsed with water and ethanol, and then dried at room temperature Carbon fibers thus obtained were rapidly inserted into a tubular furnace kept at 1000 °C and held for 5 sec to be exfoliated. ExCFs/PMMA composites were fabricated by in-situ process by polymerization. Fibrous ExCFs powder treated through ultrasonication was mixed in methyl metacrylate monomer (MMA) solution with a small amount of PMMA. And then polymeric initiator, tri butyl borane (TBB) was also added its solution for polymerization. Fabrication of the composite of ExCFs with amount of 0.5 1.0 2.0, 3.0 and 4.0 wt% were attempted, respectively. Its prepared specimens were cut longitudinally with diamond-blade saw and surface was polished into mirror surface. Final size of specimen was 4 x 4 x 50 mm. The bending strength and tensile test was measured by three-point method with a span 16 mm and a cross-head speed 0.1 mm/min. Vickers indentation, using loads of 4.9 N, was used to determine the fracture toughness. SEM was used to observe the micrograph of the mixture resin and ExCFs, and to observe the fracture surface and the micrographic crack propagation.

Results and Discussions

Additive advantageous effect of ExCFs to mechanical properties was examined and shown in Fig. 1 and 2. The flexural strength and modulus increased with the addition of ExCFs. This flexural strength and modulus of the ExCFs composite, compare with the bulk, were enhanced 166 % and 171 % at addition of only 2.0 wt% of ExCFs, respectively. On the other hand, additive advantageous effect of CNT was not recognized at addition of 2.0 wt% and its mechanical properties rather lowered.

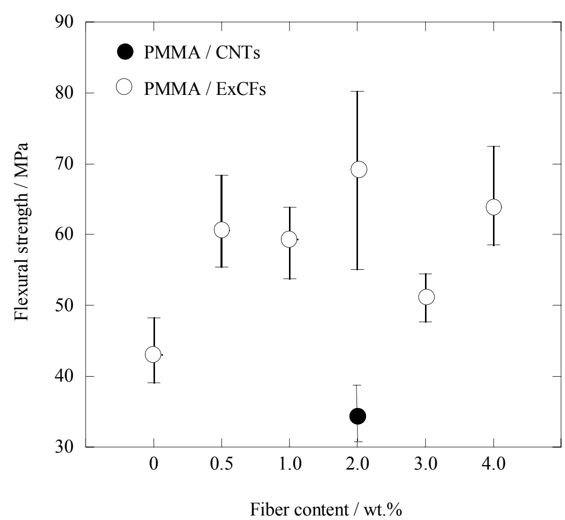

Figure 1. Dependence of fiber content of PMMA/ExCFs and PMMA/CNTs composite for flexural strength

Comparison of flexural strength and modulus of PMMA/ExCFs and PMMA/CNT at addition of 2.0 wt% by three point bending tests were summarized on Table 1. In terms of mechanical properties, ExCFs may be even better than CNT. The ExCF have large aspect ratio. According to the theory of short fiber reinforced composite, it could be improve the mechanical properties greatly.

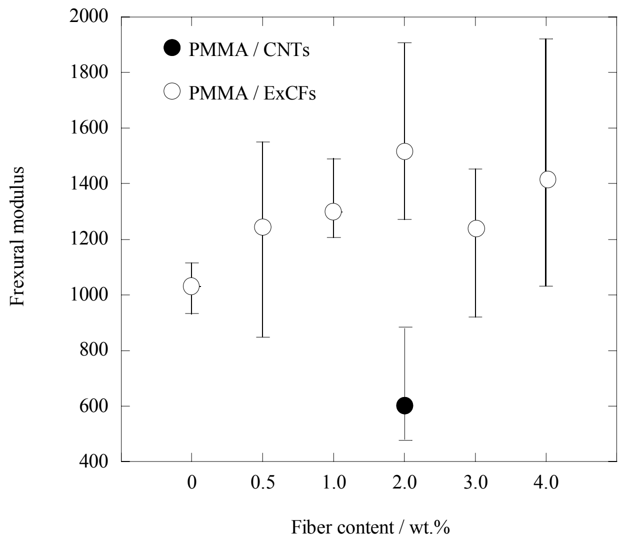

Figure 2. Dependence of fiber content of PMMA/ExCFs and PMMA/CNTs composite for flexural modulus

Table 1 Comparison of flexural strength and modulus of PMMA/ExCFs and PMMA/CNT at addition of 2.0 wt% by three point bending tests

Sample code	Flexural strength / MPa	Flexural modulus / MPa
Bulk PMMA	43.0 ± 1.4	1030 ± 28
PMMA/ExCFs – 2.0	68.9 ± 2.7	1510 ± 69
PMMA/CNTs – 2.0	35.7 ± 1.1	639 ± 62

Fig. 3 gives a typical result for the sample containing 2.0 wt% ExCFs. No significant aggregation was found in the ftacture surface, and homogeneous dispersion of ExCFs throughout the PMMA matrix could be demonstrated. From some of SEM micrographs observation for the ExCFs composite, the protruding lines or dots suggested that the embedded ExCFS were wrapped by the polymeric matrix. Closer examinations of the ExCFs reveals a thicker layer of PMMA that seems to cover the ExCFs surface, indicating some degree of wetting and phase adhesion. Most ExCFs were observed to be broken rather than just pulled out of the matrix under cleaving the samples, which also indicates that the interconnection of the ExCFs with PMMA matrix is very strong. Better mechanical properties in flexural strength and modulus of PMMA/ExCFs composites could be due to improved dispersion of the ExCFs.

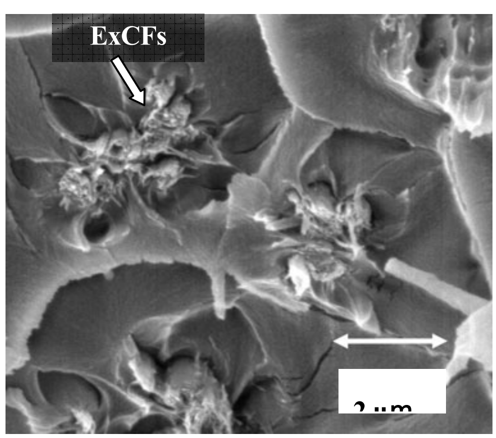

Figure 3. SEM micrograph of fracture surface of ExCFs/PMMA composite

Conclusion

ExCFs/PMMA composites have been fabricated by in-situ process with polymerization. ExCFs could be enhanced the mechanical properties of resin effectively. This flexural strength and modulus of the ExCFs composite, compare with the bulk, were enhanced 166 % and 171 % at addition of only 2.0 wt% of ExCFs, respectively. There is no significant aggregation in fracture surface, and homogeneous dispersion of ExCFs throughout the PMMA matrix was recognized. The rein forcing mechanism of ExCFs was similar with the short fiber or crystal whisker including ExCFs puling out. Homogeneous dispersion might be strongly related mechanical properties. Further improvements should be optimization of the processing procedure, so as to increase the reinforcing role of ExCFs.

References

Chen, W. 2006. Carbon nanotube-reinforced polyurethane composite fibers, *Composites Science and Technology*, 66: 3029-3034.

Toyoda, M. 2001. Exfoliation of Carbon Fibers Through Intercalation Compounds Synthesized Electrochemically,*Carbon*, 39:1697-1707.

Toyoda, M. 2001. Intercalation of Nitric Acid into Carbon Fibers, *Carbon*, 39: 2231-2234.

Toyoda, M. 2002. Intercalation of Formic Acid into Carbon Fibers and Their Exfoliation, *Synth Met.*, 130: 39-43.

Toyoda, M. 2003. Exfoliation of nitric acid intercalated carbon fibers: effects of heat-treatment temperature of pristine carbon fibers and electrolyte concentration on the exfoliation behavior, *Carbon*, 41: 731-738.

Toyoda, M. 2004. Exfoliation of Carbon Fibers, *J Phys Chem Solid.*, 65: 109-117.

Toyoda, M. 2006. Preparation of intercalation compounds of carbon fibers through electrolysis using phosphoric acid electrolyte and their exfoliation, *J. Phys. and Chem. Solids,* 67:1178-1181.

Toyoda, M. 2004. Acceleration of Graphitization in Carbon fibers through Exfoliation*, Carbon,* 42: 2567-2572.

Zhang, WD. 2004. Carbon nanotubes reinforced nyron-6 prepared by a simple melt-compouding, *Macromolecules,* 37: 25-259.