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A method for the chemical anchoring of carbon nanotubes onto carbon fibre and its impact on the strength of carbon fibre composites

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Abstract This article proposes an alternative way to use carbon nanotubes to improve the performance of carbon fibre-reinforced composites. A chemical process, based on esterification of surface groups, is used to anchor nanotubes onto carbon fibre surface. Anchored nanotubes form a network surrounding the carbon fibres. After CNT anchoring, the tow is impregnated with an epoxy resin and tensile tests are performed on this minicomposite sample. By enhancing matrix properties and fibre/matrix interface, the CNT network has a significant influence on the composite strength.

Introduction

Due to their exceptional mechanical properties, carbon nanotubes (CNT) are proposed for the reinforcement of carbon fibre-reinforced composites (CFRC). Two ways are currently being explored by research teams: dispersion of CNTs in the epoxy matrix or CVD-processing of CNTs onto CF surface. In the first article, we proposed an alternative method based on chemical bonding between CNT and CF [1]. Functionalization of CNT surface is one of the most important research areas in CNT science [2]. Among the various techniques, esterification and amidation of surface groups is commonly used [3]. Surface groups are useful to modify CNT properties like solvent solubility, biological compatibility, dispersion, etc. In particular, a sufficient concentration of oxygen-containing groups increases interfacial bond strength of fibre with polymer [4]. Surface groups are implanted on free valences of the graphite carbon atoms, these free valances are created during oxidation treatment. Our method uses surface groups to create chemical bondings between CNTs and CFs and has been completely revisited with optimisation of temperature, time, solvent, catalyst and coupling agent.

Some articles have exposed similar methods based on ester or amide bonds to create permanent links between CNTs and other kinds of particles. Shan et al. [5] anchored ZrO_2 ceramic particles onto carbon surface with ester bonding. Ogino et al. [6] developed an original procedure for the preparation of CNT film. With FTIR spectroscopy, they proved that MWCNT modified with carboxylic acid and hydroxyl groups was cross-linked through ester bondings. Tensile and Vickers hardness tests of cross-linked films show significantly improved results compared to films without ester bondings. He et al. [7] adapted an anchoring method from Kevlar fibre technology. They functionalized end caps-MWCNTs with hexamethylenediamine and CFs with acyl chloride. XPS analysis confirmed formation of covalent bondings. CNTs are uniformly distributed at the CF surface with a CNT weight fraction of 1.2%. To attach CNTs on Pt electrode, Rosario-Castro et al. [8] functionalized CNTs with carboxylic groups by acid treatment and Pt electrode with amino-terminated groups. With Infrared and X-ray spectrocopies they also observed creation of amide bondings between CNT and Pt surfaces.

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Experiment

Anchoring of CNTs onto CF surface

Industrial T700S carbon fibres are used in this study. A CF tow is composed of 12,000 individual fibres, 7 µm in diameter. CF tow of 250 mm in length is cut from a commercial reel. CF unsizing is carried out in an oven under nitrogen at 450°C for 15 min. This first step is followed by CF oxidation at 450 °C under air for 30 min. During this step, carboxylic and hydroxyl groups are created on CF surface [9]. Generally, surface groups are implanted on CF surface to improve interfacial bond strength between CF and polymer matrix [4]. Here, surface groups are useful for chemical bonding between CFs and CNTs.

Multi-wall type carbon nanotubes are synthesized by the CVD method [10]. Their average diameter varies from 50 to 100 nm and their length from 1 to 4 µm. As-received CNTs are functionalized in a mixture of concentrated sulfuric and nitric acids. FTIR analysis of CNT confirms that functionalization creates carboxylic and hydroxyl groups on CNT surface [1].

Carbon nanotubes anchoring is made by an esterification between the carboxylic and hydroxyl groups on CF and CNT surfaces. The esterification follows the Steglich method and uses dicyclohexylcarbodiimide (DCC) as a coupling agent and 4-dimethylamino-pyridine (DMAP) as a catalyst [11].

The first solution containing 10 mg of CNT dispersed in 50 ml of dichloromethane with 6.43 mg of DCC is prepared and maintained under sonication. Contrary to our first article [1], we have preferred dichloromethane to acetone as a solvent because DCC is highly soluble in dichloromethane and acetone could react with the carboxylic group. 11.61 mg of DMAP are dispersed in a second solution of 50 ml of dichloromethane.

After thermal treatment, the CF tow is spread on a glass substrate. The first CNT solution is deposited drop by drop over the entire length of the tow. The second solution is then deposited in the same way. The tow is maintained at 20 °C for 1 h and then dried in an oven at 100 °C for 1 h. The anchoring treatment is followed by intensive washing to eliminate un-anchored CNTs and residues of chemical solutions from the tow. CF tows are weighed before and after the anchoring treatment with a high-precision scale (Mettler Toledo XS105 with an accuracy of 0.01 mg). Each sample was weighed five times to obtain a mean value.

The different micrographs (CF surface, CNT network, tensile test specimen) have been made with a JEOL 6400 Scanning electron microscope without gold plating.

Minicomposite specimen for tensile tests

A special mould has been designed to obtain regular specimens for tensile tests (Fig. 1a). Minicomposite specimen, comprising one single tow, is one-dimensional composite useful to characterize easily and rapidly mechanical performances of modified fibre. After anchoring treatment, only the central part of each tow is used for composite sample manufacturing, 160 mm in length. As sample width is equal to 3 mm, sample thickness is adjusted by the compression of elastic springs with screws and is fixed at 0.4 mm to obtain a value of 40% for the fibre volume fraction. After tow impregnation by an epoxy matrix, bisphenol A type associated to a low-reactivity amine hardener, the polymerization cycle begins with a 12 h stage at room temperature followed by a final 4 h curing at 100 °C. It should be noted that, after mixing and prior to tow impregnation, the epoxy resin is degassed in a vacuum chamber for 1 h to extract air bubbles formed during epoxy mixing.

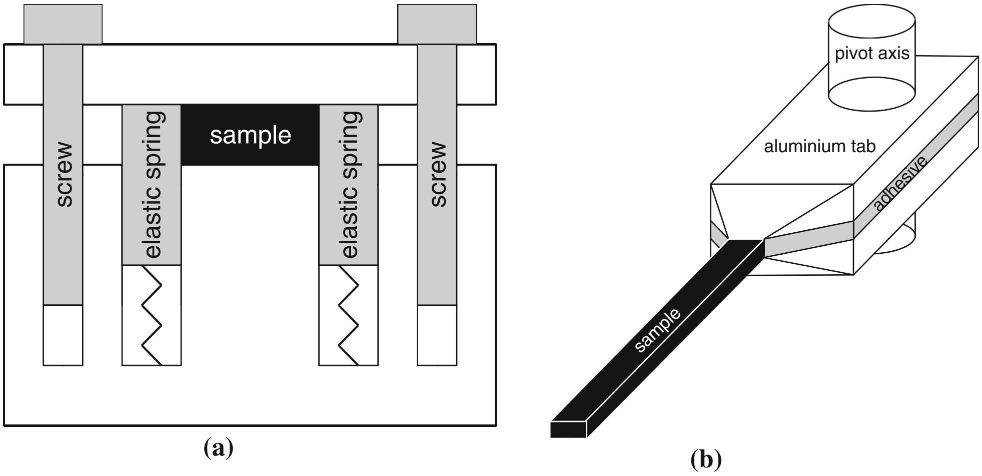

Fig. 1 **a** Sectional view of minicomposite mould. **b** End-tapped tensile specimen

Once the sample is cured, each extremity is pasted between two aluminium tabs with a high shear resistant adhesive (Fig. 1b); minicomposite gauge length is equal to 80 mm. To minimize parasite bending moment and to facilitate specimen alignment, a pivot axis, with a cylindrical joint, is integrated in the tabs. Tensile tests were conducted on a servo-hydraulic testing machine (Instron 8801), equipped with a 5 kN load captor. All the tests were performed at room temperature with a testing speed of 0.5 mm/min.

Results and discussion

Thermal stability of carbon fibre

The thermal and oxidation treatment is necessary for CF unsizing and the creation of carboxylic and hydroxyl groups on CF surface. These groups are the basis of the ester bondings between CNTs and CFs. However, thermal treatment is known to be a source of degradations of carbon fibre structure and properties.

The thermal stability of the carbon fibres has been investigated by Thermogravimetric Analysis (TGA) (Perkin-Elmer TGA 7), at a 10 °C/min heating rate in nitrogen and in air. Under nitrogen, CF mass decreases gradually between 100 and 420 °C to 97.1% of the initial mass (Fig. 2). This 2.9% mass loss corresponds to the degradation of the sizing that is a thin layer of organic polymer. It should be noted that this value is superior to the usual value of 1–1.5%. At 580 °C a new phase is started, mass decreases slightly and progressively, reaching 96.6% of the initial value at 900 °C. Under air, carbon fibres are not thermally stable [12]. During the first stage, between 96 and 395 °C, thermal behaviour is roughly similar and the mass loss is limited to 1.2%. At 520 °C, the CF combustion occurs and is completely finished at 850 °C.

To refine these results, the complete thermal treatment has been reproduced in the TGA apparatus. During the first stage, the temperature is increased from 50 °C to the treatment temperature (450, 500 or 600 °C) and the atmosphere is nitrogen. After 15 min, the atmosphere is switched to air for a period of 30 min. The sample mass is monitored all over the treatment (Fig. 3).

Whatever may be the treatment temperature (450, 500 or 600 °C), the sample mass decreases during the first treatment step under nitrogen. This mass loss of about 1.5% corresponds to CF unsizing. With a treatment temperature of 600 °C, when atmosphere is switched to air, the CF undergoes a constant degradation. At 450 and 500 °C, the CF mass remains constant. Moreover, compared to fibre treated at 450 °C, SEM micrographs of 600 °C treated fibre reveal explicit degradations of CF surface (Fig. 4). At 600 °C, numerous stitches and pores are present on CF surface whereas, at 450 °C the CF surface remains smooth. Oxidative treatment preferentially occurs at the amorphous regions of CF surface [4, 13]. When thermal treatment is too intensive, oxidation extends to crystallized regions. Some graphite particles are pulled, creating pores and pitting.

To complete the evaluation of the impact of thermal and anchoring treatment, CF mechanical properties have been evaluated with minicomposite sample tensile tests. Minicomposite specimen made with as-received fibres with sizing are compared to composites made with fibres that have undergone the complete thermal and CNT anchoring treatments, but with solutions containing no CNTs.

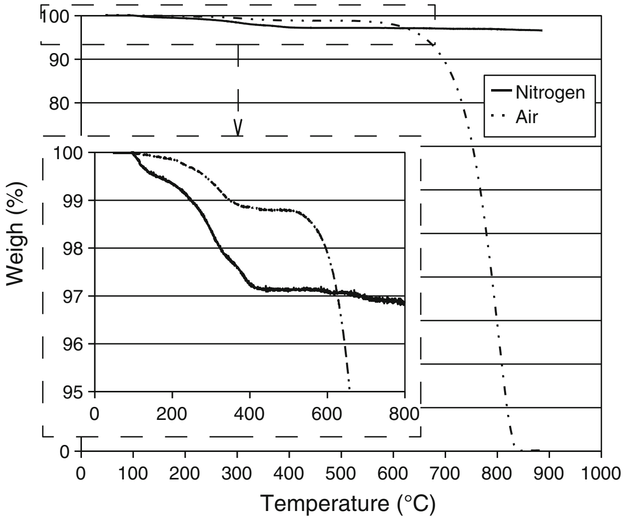

Fig. 2 Thermal stability of carbon fibre examined by Thermogravimetric analysis

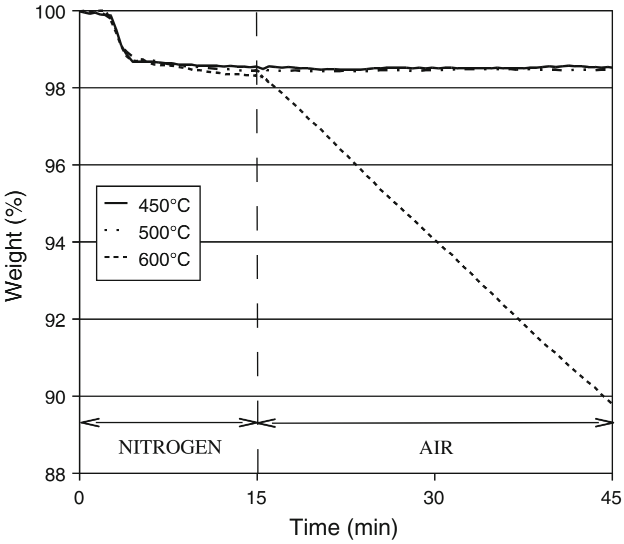

Fig. 3 Evolution of CF mass during unsizing and oxidation treatment for various treatment temperatures measured by TGA

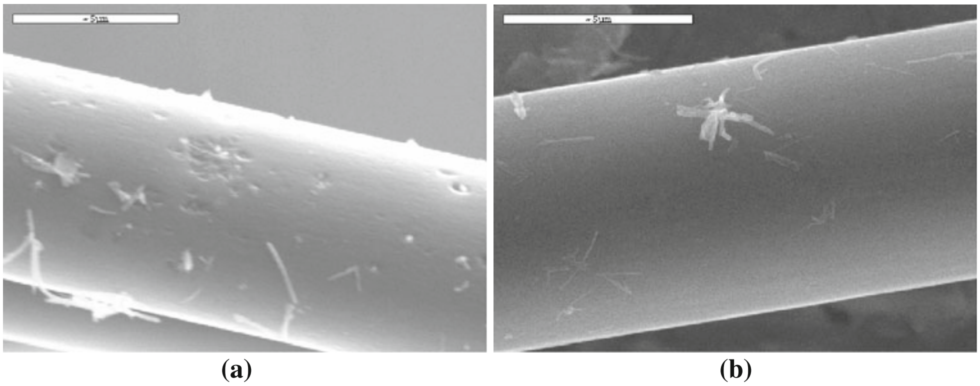

Fig. 4 SEM micrographs of CF after thermal treatment **a** 600 °C and **b** 450 °C. The micrographs have been made after CNT anchoring treatment

Ultimate tensile strength of sized CF composite samples is estimated at 1,450 MPa, with a standard deviation value of 270. For 450 °C treated fibres, CFRC strength collapses to 680 MPa, standard deviation value of 115. We suppose that, even if mass loss is reduced at 450 °C and SEM micrographs have not revealed pitting on CF surface, thermal treatment creates some new defects in CF structure. These defects increase dramatically the CF strength.

Impact of CNT network on the strength of carbon fibre reinforced composites

The anchoring rate of CNTs on the CF tow is measured by the evolution of CF weight during the chemical treatment. The CNT mass rate, on the CF tow mass, varies from 0.17 to 1.36%, with a mean value of 0.76%. CNTs form a network surrounding the carbon fibres (Fig. 5). Obviously some CNTs are not anchored onto the CF surface, but are mechanically interlocked in the CNT network. The CF covering is not complete and some parts of the fibre are not covered by CNTs. Even if the tow is carefully spread on the glass plate, the fibres filter CNTs that can have difficulty in penetrating the tow [14]. Moreover, during thermal treatment, a fibre can be covered by other fibres. Consequently some areas are not oxidized.

Fibre distribution in minicomposite samples is not homogeneous as revealed by observation of the fracture surface (Fig. 6). Composites are composed of rich and poor fibre areas. We suppose that high-density fibre areas are related to groups of fibres linked by CNT networks.

The volume fraction of nanotubes within the composite is calculated from the mass rate of nanotube grafted onto fibres and on the assumption that CF and CNT densities are equal ($\rho_{\mathrm{CF}} = 1800$ kg/m^3, $\rho_{\mathrm{epoxy}} = 1230$ kg/m^3). As CF volume fraction is around 40%, the CNT volume fraction is very low, between 0.05 and 0.49%, with an average of 0.30%.

CFRC tensile strength changes significantly when CNTs are anchored onto CF surface (Fig. 7). Strength increases by 62% for a CNT volume fraction of 0.5% and reaches the value of 1,100 MPa (680 MPa for reference samples). It should be noted that the reference samples, with a CNT volume fraction equal to 0%, have undergone the complete thermal and chemical treatments, but with solutions containing no CNTs.

Reinforcement mechanisms of the mechanical properties of CFRC modified with CNTs are mainly dependent on CNT morphology. Initially, Downs et al. [15] and Thostenson et al. [16] have grown by CVD a dense forest of short nanotubes or nanofibres on single carbon fibre. Downs et al. obtained an improvement over 4.75 times of

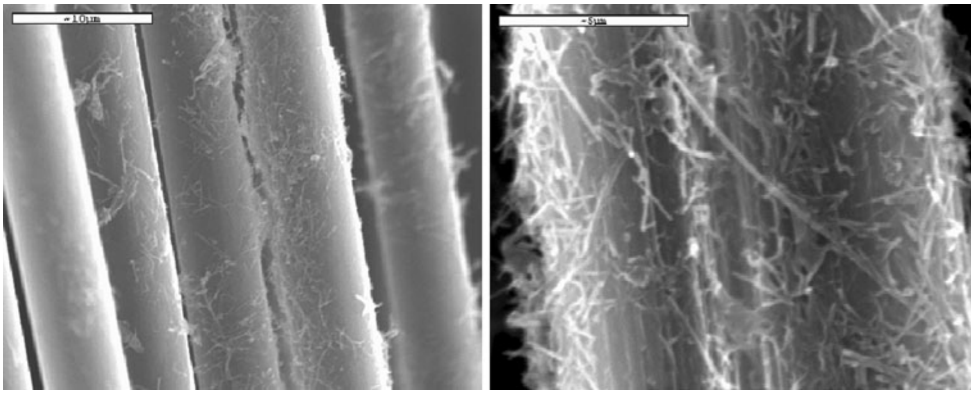

Fig. 5 SEM micrographs of anchored CNTs on CF surface and bonding between two CFs

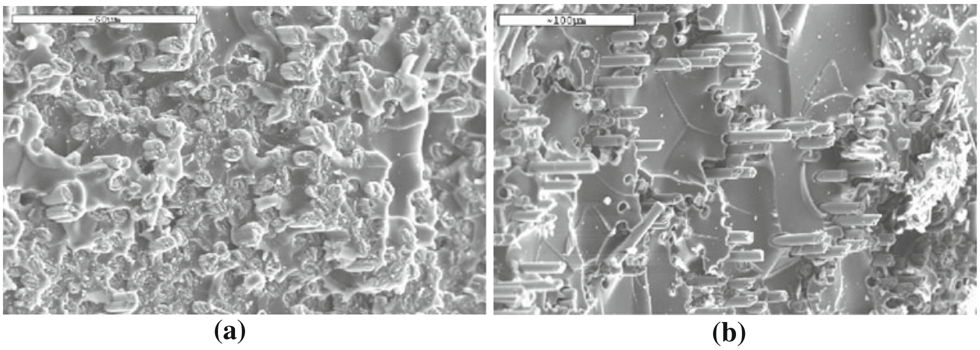
(a) (b)

Fig. 6 SEM micrographs of fracture surfaces of minicomposite. Rich (**a**) and poor (**b**) fibre areas

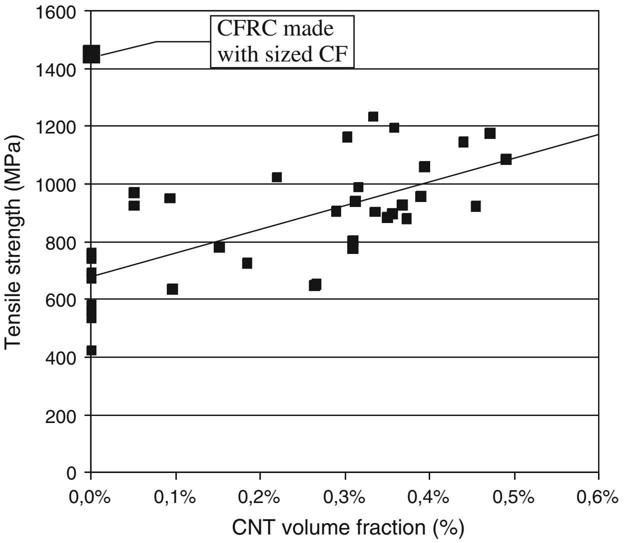

Fig. 7 Composite tensile strength versus CNT volume fraction

the interfacial strength with a polyvinylethylacetate matrix [15], while the improvement is limited to 15% with an epoxy resin [16]. Secondly, longer CNTs increase the efficiency of load transfer between CF and the matrix by a harpoon effect [17]. Moreover, with high CNT volume fraction, CNT networks are interlaced and they improve internal cohesion and matrix properties [18]. Load transfer between fibres and matrix is increased. As a consequence crack initiation and propagation are limited which leads to enhancement of the composite strength.

However, with a strength of 1,450 MPa for composite made with the original sized fibre, the gain provided by the nanotubes is not sufficient to offset the loss of properties caused by fibre thermal degradation. The fibre preparation treatment is too aggressive and must be softened. The better solution should be to integrate the CNT anchoring treatment during the CF synthesis process. Indeed, all our tests have been carried with commercial sized fibres and the first step was to unsized the fibres, that involve some fibre degradations. Integration of CNT anchoring into the fibre synthesis process would eliminate the unsizing-oxidation phases. Moreover, in an industrial process grafting could be done in successive chemical baths with a continuous passage of fibres. The fibres would then be better treated by the CNT solutions, and CNT grafting would cover the entire surface of fibres without CNT low-density areas. In this case, CNT network would become a real opportunity to emphasize CFRC properties.

Conclusion

Carbon nanotubes are anchored onto carbon surface using a chemical process. This process is based on the esterification of carboxylic and hydroxyl groups created onto CNT and CF surface by an oxidation treatment. The esterification follows the Steglich method and uses dicyclohexylcarbodiimide (DCC) as a coupling agent and 4-dimethylamino-pyridine (DMAP) as a catalyst.

The CNT mass rate varies from 0.17 to 1.36%, with a mean value of 0.76%. CNTs form a three-dimensional network surrounding CFs. After chemical anchoring, CF tows are impregnated with an epoxy resin to obtain minicomposite samples. As CNTs are homogeneously dispersed all over the CF tow, initially the matrix is stiffer and secondly interfacial strength is enhanced. The fibres are shielded from crack propagation and the composite tensile strength is improved.

Although CNT networks have a significant and reinforcement effect, fibre preparation treatment (unsizing-oxidation) produces some significant degradations of the fibres. Even if CF oxidation treatment induces a weak mass loss, limited to 1.5% of the initial CF mass, CF strength is significantly affected and is divided by 2. To fully benefit from the CNT effect optimization of fibre preparation treatment seems to be necessary.

References

1. Laachachi A, Vivet A, Nouet G, Ben Doudou B, Poilâne C, Chen J et al (2008) Mater Lett 62(3):394
2. Balasubramanian K, Burghard M (2005) Small 1(2):180

3. Tasis D, Tagmatarchis N, Georgakilas V, Prato M (2003) Chem Eur J 9(17):4000
4. Tang LG, Kardos JL (1997) Polym Compos 18(1):100
5. Shan Y, Gao L, Li X, Yu X, Chen K (2008) MRS international material research conference 2008. Chongqing, China
6. Ogino S, Sato Y, Yamamoto G, Sasamori K, Kimura H, Hashida T et al. (2007) In: 4th International workshop on water dynamics, AIP conference proceedings 2007, vol 898, p 175
7. He X, Zhang F, Wang R, Liu R (2007) Carbon 45(13):2559
8. Rosario-Castro BI, Contés EJ, Pérez-Davis ME, Cabrera CR (2005) Rev Adv Mater Sci 10:381
9. Park SJ, Kim BJ (2005) Mater Sci Eng A 408(1–2):269
10. Bai S, Li F, Yang QH, Cheng HM, Bai JB (2003) Chem Phys Lett 376:83
11. Neises B, Steglich W (1990) Org Synth 7:93
12. Xu Y, Cheng L, Zhang L, Yin H, Yin X, You C (2001) J Eur Ceram Soc 21:809
13. Fukunnaga A, Ueda S (2000) Compos Sci Technol 60:249
14. Fan Z, Hsiao KT, Advani S (2004) Carbon 42(4):871
15. Downs WB, Baker RTK (1996) J Mater Res 10(3):625
16. Thostenson ET, Li WZ, Wang DZ, Ren ZF, Chou TW (2002) J Appl Phys 91(9):6034
17. Hung KH, Kuo WS, Ko TH, Tzeng SS, Yan CF (2009) Compos Part A 40(8):1299
18. Zhou Y, Pervin F, Lewis L et al (2008) Mater Sci Eng A 475:157