Thermo-mechanical stability of epoxy composites induced with surface silanized recycled carbon fibers

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Abstract. Epoxy composites were prepared using surface silanized chopped carbon fibers (CCFs). Silanized CCFs were synthesized from industrial waste carbon fibers. This work demonstrates the capability of surface silanized chopped carbon fibers to enhance the thermo-mechanical stability of the epoxy composites. The surface silanization of the CCFs to amend the interfacial interaction with epoxy network was done by attaching siloxane functional groups onto CCFs surfaces. Epoxy composites blended with 0.5 and 1 wt % of siloxane decorated CCFs showed a tremendous enhancement in storage modulus in comparison to neat epoxy. This enhancement of composites properties opens up the scope to utilize CCFs for high performance and cost effective epoxy composites. This study opens up the use of juvenile CCFs from waste carbon fibers for their utilization in next generation composites.

1. Introduction
The use of carbon fiber reinforced plastics (CFRPs) made from continuous carbon fibers (CFs) has gained an increasing demand in aerospace, energy, marine and automobile industries due to their outstanding properties such as preeminent mechanical strength and stiffness, lower density, flexible designs and chemical stability [1-2]. In spite of all merits related to CFRPs, the increasing demand leads to an increasing amount of manufacturing waste, which is around 40% of such composite waste, whereas, woven trimmings hold more than 60% to this number [3-4]. The wastage of CFs is an added economic loss to the industries due to the high production cost of CFs (up to 40 £/kg) [5-7]. Therefore, the industries are recycling the waste CFs to mitigate their economic loss [8, 9].

Short CFs recycled from waste are being used as reinforcement in the epoxy resin for fabricating composites which can give low cost alternative materials in modern material market due to its light weight and high strength [5, 7]. The epoxy resin is one of the promising polymer which is increasingly used in wide range of automotive and aerospace applications due to its high adhesive property, high strength and hardness [10, 11]. However the highly cross-linking of epoxy matrices leads to a high brittleness and poor resistance to crack initiation and growth [12-14] which may affect the overall fatigue and fracture performance of epoxy resin. Moreover, epoxy resin fails spontaneously due to local stress concentration which initiates the crack [12]. Though, many works have been reported recently for short CFs (CCFs) in thermoplastics polymer but very few works have been reported for epoxy resin [15, 16]. Moreover, the chemically inert surface and low surface energy [15-17] of CFs can hinder the interfacial adhesion with epoxy resin and hence lower the efficiency of CCFs as filler materials in epoxy resin. The chemical modification of CFs surface can enhance the compatibility of it...
with epoxy resin. Although various surface treatments (gaseous oxidation, electrochemical oxidation, liquid oxidation, plasma oxidation, surface grafting, polymer sizing) are used to modify the CFs surfaces [18, 19], but liquid oxidation is found one such common method [17] to functionalize the CF surface for their ease to produce functional group into CF surfaces. The functional group produced from oxidation does not react chemically with epoxy resin at low temperature [20], rather, oxidation sometimes reduces the strength of CFs [18,17]. To overcome this problem, silane coupling agents can be used further to modify the oxidized CF surfaces [18]. The silane coupling agent reacts with carboxyl groups on CF surfaces produced through oxidation [16, 18]. The siloxane grafting of carbon fiber again covalently bonded with epoxy resin which improve the interfacial adhesion and hence expected to enhance thermo-mechanical properties of epoxy composite.

The main aim of this current research work is to produce CCFs from industrial waste CFs and surface silanization of produced CCFs using (3-Aminopropyl)triethoxysilane. This silanized CCFs is induced in epoxy matrices to prepare CCF-epoxy composite to evaluate its thermo-mechanical properties. This work is expected to espouse the use of CCFs as an efficient reinforcement for strengthening of epoxy resin.

2. Materials and methods

Waste Polyacrylonitrile (class: AS4; Hexcel Composite, France) based carbon fibers (CFs) were collected from National Aerospace Laboratories, India. The waste carbon fibers are shown in figure 1 (a). Firstly, waste CFs were mechanically chopped to fibers having ~5 mm length (figure 1 (b)) and subsequently washed in deionized water and vacuum dried at 80 °C for 8 h. These fibers were further grounded in aged mortar to prepare CCFs (Figure 1(c)). These CCFs were cleansed by using soxhlet extraction process with DCM at 60 °C for 24 h followed by vacuum drying at 80 °C for 8 h and named as pristine CCFs (P-CCFs). The figure 1(d) shows the FESEM analysis of P-CCF.

In the second step, ~0.3 g of P-CCFs was reacted with 20 ml of conc. HNO₃ for 1.5 h at 80 °C under continuous stirring at 600 rpm. Oxidized CCFs (O-CCFs) were obtained by washing and filtering with distilled water, ethanol and acetone till pH 7 was achieved followed by vacuum drying at 80 °C for 8 h. In third step, O-CCFs of ~0.3 g of O-CCFs was introduced in a round bottom flask containing 25 ml of toluene and placed in a bath sonicator for 1 h. A premixed solution of dissolved APTES (1 wt% of O-CCFs) in 5 ml toluene was then drop-wise added into the above mentioned toluene solution and the resulting solution was further refluxed at 110 °C for 8 h with continuous stirring at 600 rpm. Silanized CCFs (S-CCFs) were obtained after washing several times with distilled water, ethanol and acetone in sequence and vacuum dried at 80 °C for 8 h.

To make epoxy composites, 0.5 and 1.0 wt% of P-CCFs and S-CCFs were mixed with epoxy resin (Lapox L-12, Atul Ltd). Both the P-CCFs and S-CCFs are dispersed into the epoxy resin and allowed
to completely wet the CFs without any disturbance. Then the wet solution is mechanically stirred for 30 min at 1500 rpm using REMI LAB STIRRER (Model: RQT-124A/D, Motor: AC/DC 1/8 HP, Max speed: 4000 rpm) as shown in figure 2 (a). The resulting solution then degassed at vacuum desiccator attached with vacuum pump to remove the entrapped air as shown in figure 2 (b). All operations are carried out at room temperature. Later, curing agent (Lapox K-6) was added and mechanically mixed for another 5 minutes under room temperature and degassed further. This mixture was poured into silicon mold and cured in room temperature for 24 h. similar process is followed for preparing neat epoxy (NE) without any filler.

### 3. Results and discussion

The proof of successful silanization of CCFs are given in our recent publication and the details characterization technique are also provided there [21]. The thermo-mechanical stability of epoxy composites was investigated under dynamic mechanical analyzer (DMA) to determine the effectiveness of P-CCFs, S-CCFs onto epoxy resin to access their loading capability in glassy and rubbery state as shown in figure 3. Significant variation in storage modulus (E’ (MPa)) due to the addition of silanized CCFs in epoxy network with respect to NE in the glassy region is evident from figure 3 (a). At the glassy region (35 °C) the E’ for NE is ~148 MPa, which has been enhanced to ~569 MPa and ~702 MPa due to addition of 0.5 and 1 wt% of P-CCF. This finding endorse the stiffening effect of CCFs which helps to enhance the stored energy of epoxy composites. On the other hand, S-CCFs shows tremendous impact on the stiffness and molecular relaxation of S-CCFEC. The E’ is found as ~702 and 791 MPa for 0.5 and 1 wt% addition of S-CCF. Hence, giving a significant enhancement in E’ of ~376% and ~434% respectively compared to that of NE. In case of epoxy composites induced with silanized CCFs, the epoxide groups reacted covalently with the amine (NH₂) groups attached to the S-CCFs during silanization reaction [21], thereby, enhances the storage modulus. However, at high temperature, the effect of silanization on composite modulus is negligible.
This is possibly attributed to their higher molecular motion and vibration at high amplitude in the rubbery region [22, 23].

Mobility behavior of the epoxy composite is further investigated from the position and intensity of loss factor \((\tan \delta)\) as shown in figure. 3 (b). The glass transition temperature, \(T_g\) of the epoxy composites is taken from the temperature axis corresponding to the peak of \(\tan \delta\) plot. The addition of P-CCFs, S-CCFs at 0.5 epoxy network lead to decrease in \(T_g\) as compared to NE as can be seen in figure 3 (b). Moreover, a large variation in intensity of \(\tan \delta\) peak can be observed for the composites. This enlightens the difference in the epoxy network characteristics of NE, P-CCFEC, and S-CCFEC. Hence, incorporation of pristine and silanized CCFs at 0.5 wt% may have imbalanced the curing stoichiometry and thereby hinders the curing process of epoxy network which might be affecting the crosslinking density of final composites [24–25]. The decrease in \(T_g\) due to improper curing stoichiometric is also reported in other refs. [24, 26]. Furthermore, the increased intensity of \(\tan \delta\) for P-CCFEC, and S-CCFEC compared to the NE indicates the relatively viscous responses to stress. Though, S-CCFs covalently linked with epoxy network, the increased height of \(\tan \delta\) peak compared to the NE may have arisen from the greater number of flexible Si-O-Si linkages as discussed by Das et al. [21]. Whereas, the addition of P-CCF and S-CCF at higher wt% above 0.5 wt%, helps to reduce the peak height of \(\tan \delta\) and enhances the \(T_g\) owing to the restriction of overall epoxy network.

4. Conclusion

CCFs were prepared from waste carbon fibers. The pristine CCFs were further modified by organosilane by attaching highly active siloxane functional groups for better interaction with epoxy network. The incorporation of surface silanized CCFs in epoxy network significantly affect the molecular relaxation behavior of final epoxy composites. The incorporation of 1 wt % of S-CCFs in epoxy resin shows potential improvement in the storage modulus with ~434% enhancement as compared to that of NE due to formation of covalent bonding between S-CCFs and epoxy network.

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