

Effects of various chemical treatments on physicochemical properties of cotton shell fibers –A study

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Abstract

The hydrophilic characteristic of natural fibers was mostly caused due to the existence of hemicellulose and lignin contents which are diminished by carrying out various chemical treatments. The adhesion property and mechanical properties are enhanced due to the chemical treatments. The optimally alkali treated Cotton Shell Fibers (CSFs) were subjected to chemical modifications by using Benzoyl Chloride, Potassium Permanganate, Stearic Acid and Zinc Chloride. From the alkaline treatment, 5 % (w/v) NaOH solution with 60 minutes soaking time was established as optimum. In continuation with alkali treatment, chemical modifications were done and the thermal analysis, X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy reports confirm positive changes in the physicochemical properties of CSFs and also successful elimination of amorphous and wax contents.

Key words

Chemical treatments, Cotton Shell Fibers, Crystallinity Index, FTIR spectroscopy, Thermal analysis

INTRODUCTION

Natural fibers offer an alternative to the synthetic fibers due to their low cost, low density and biodegradability. A better understanding of fiber-matrix interface and the ability to transfer stress from the matrix to the fiber is essential for manufacturing natural fiber-reinforced composites. Chemical treatments are believed in modifying the fiber surface properties because it can improve the bonding strength between fiber and matrix, due to differential hydroxyl group and also give resistance in moisture absorption capacity of the natural fiber. Also the chemical treatments of natural fibers were used for eliminating impurities and to get improved fiber – matrix interaction.

Great pain have been taken by many researchers and scientists to alternate synthetic fibers with biodegradable natural fibers to use effectively these fibers in many applications specifically in manufacturing polymer composite materials ^[1].The degree of adhesion among the fiber and matrix decides the mechanical properties of the natural fiber reinforced composites. Inadequate fiber/matrix interface promotes weaker material with low strength and less life span. So, the researchers focus is on

maintaining the better interfacial adhesion by carrying out physical and chemical treatments to change them most compatible with matrix. The processes also enhance durability and wear resistance of the composites [2].

The strong polarity of natural fiber is the major disadvantage for it, which leads to poor interfacial bonding among the fiber and matrix. Again this leads to weak properties to the natural fiber reinforced polymer composites. This problem is rectified by chemical modification of natural fibers as this process make these fibers less hydrophilic and thereby it form strong compatibility between fiber and matrix [3]. The various chemical treatments such as alkalination, acetylation, permanganate, silane, peroxide, acrylation and isocyanate treatments have successfully achieved the favourable improvements in the fiber strength, stiffness and fiber adhesion in natural fiber reinforced composites [4]. The various chemical treatments converts the natural fibers more porous in nature to resin while used as reinforcement [5].

Natural fibers are changeable to chemical modification because of the existence of hydroxyl groups. Inside the cellulose molecules, the hydroxyl groups are concerned in hydrogen bonding thereby activating these groups will develop efficient interlocks within the system. Chemical modifications enhance the fiber surface characteristics like adhesion, wetting and porosity. By adopting suitable chemical modification the interfacial properties may be enhanced that develop the amendment in physical and chemical interactions at the interface [6]. The improved chemical interlocking and better adhesion at the interface of fiber and matrix were achieved by permanganate treatment [7]. The stress transfer efficiency at the interface was enhanced due to the two chemical treatments, acetylation and stearamation to flax fibers [8].

Almost all the fields start to apply the natural fiber –reinforced composites. Recently the ligno-cellulosic natural fibers are utilized as reinforcement in polymer composite materials for construction panels, furniture and as well as automobile parts as they have excellent physical and mechanical properties [9].

The aim of this present investigation is to study the influence and effect of various chemical modifications carried out on alkali pre-treated CSFs. The related reports are established by conducting thermal analysis for finding fiber degradation temperature, X-ray diffraction technique for monitoring the crystallinity index improvement. Also by using FTIR analysis the enhancement of adhesion between the fiber and matrix and increase in mechanical properties are assessed.

EXPERIMENTAL PROCEDURE

Materials

Cotton shell (CS), a fibrous by-product of cotton plant (*Gossipium arboreum*), belong to Malvaceae family, were procured from local resources in and around Kovilpatti, Tamilnadu, India. Single harvest CS raw materials were preferred for this investigation. The analytical grade of Sodium hydroxide pellets (98% strength), was used for pre-treatment. Reagent grade chemicals Benzoyl Chloride, Potassium Permanganate, Stearic Acid and Zinc Chloride were obtained from Modern scientific company, Madurai, Tamilnadu, India, and as used.

Extraction and preparation of CSFs for Alkali treatment

Initially, to remove the dust and impurities present in the raw CS, they were rinsed in water. The fibers from raw CS were extracted by manual peeling, before that they were immersed in water for 2-4 hours. The CSFs were again washed with distilled water several times and then dried in an oven at 50° C for 24 hours.

CHEMICAL TREATMENTS OF OPTIMALLY TREATED CSFS

Optimally Alkali treated CSFs (Optimal ACSFs)

Before conducting the chemical modifications of natural fiber it is appropriate to have alkali pre-treatment for better results. The alkali treatment of CSFs was carried out with 5 % (w/v) NaOH solution and found 45 minutes soaking time as optimum ^[10]. The destruction of hydrogen bonding in the hydroxyl groups by alkali treatment, converts the unreactive cellulose hydroxyl group in the fiber in to more reactive ^[25]. The limitations must be overcome, so as to exploit the full potential of natural fibers, that is exactly done by an appropriate fiber surface treatment ^[26]. The surface amendment of natural fibers is mandatory to create them less hydrophilic ^[27]. These fibre surface amendments can progress fibre-matrix interfacial bonding, roughness, wettability and can decrease moisture absorption, which can augment the tensile properties of plant fibers ^[28].

Benzoyl Chloride –treated CSFs (BCSFs)

The optimally alkali treated CSFs were soaked in 6 % NaOH and stirred with benzoyl chloride solution for 30 minutes^[2,3, 7, 11-13]. Then the separated CSFs were immersed in ethanol for one hour to eliminate the benzoyl chloride and washed with deionized water and dried in an oven at 50° C for 24 hours.

Potassium Permanganate –treated CSFs (PCSFs)

The optimally alkali treated CSFs were soaked in 0.5 % potassium permanganate (KMnO₄) in acetone for 30 minutes [3, 7, 14, 25].

Stearic Acid – treated CSFs (SCSFs)

The optimally alkali treated CSFs were soaked in 1 % stearic acid dissolved ethyl alcohol solution for 30 minutes. Then the isolated fibers were dried in an oven at 50° C for 24 hours^[14].

Zinc Chloride –treated CSFs (ZCSFs)

The optimally alkali treated CSFs were soaked in 3 % Zinc chloride solution for 30 minutes. Then the isolated fibers were dried in an oven at 50° C for 24 hours^[15].

Thermal analysis of alkali treated CSFs

Thermal analysis of chemically treated natural fibers provides the detail, which is used to characterize the disintegration and thermal stability of the fiber materials. TGA and Differential Thermogravimetry (DTG) studies of the chemically modified CSFs were exposed in Nitrogen atmosphere in thermal analyzer, (Jupiter, NETZSCH, Germany, Model STA 449 F3) at a heating rate of 10° C per minute over a temperature range from ambient temperature to 600° C.

XRD analysis

The X-ray diffraction data are noted after mounting the chemically modified CSFs in powdered form on a sample holder. Using X'Pert PRO diffractometer with Bragg–Brentano parafocusing geometry, a monochromatic diffracted beam, and a copper target X-ray tube set with 40 kV and 30 mA power, X ray wavelength $\lambda = 1.5406 \text{ \AA}$, over a range of $10^\circ \leq 2\theta \leq 80^\circ$ XRD analysis was performed.

Evaluation of Crystalline index (CI)

From the X-ray diffractogram, the degree of Crystallinity or Crystalline Index (CI) in the cellulosic materials is calculated according to the peak height method developed by the following Segal empirical equation.

$$CI = \frac{(I_{200} - I_{AM})}{I_{200}} \quad (1)$$

Where I_{200} represents the maximum intensity of the 200 lattice plane at a 2θ angle between 22° and 23° and I_{AM} represents the intensity of non crystalline or amorphous material measured by height of the valley of the minimum between the peaks, at an angle of 2θ about 16° .

FTIR analysis

FT-IR spectroscopic analysis of chemically treated CSFs was performed with Perkin Elmer (FTIR – 4600 type A, USA) with an accumulation of 32 scan with the resolution of 4 cm^{-1} in the scanning range of wave number region between 4000 cm^{-1} and 400 cm^{-1} , with a scanning speed of 2 mm/sec . Approximately two milli grams of chemically modified CSFs were ground manually to micro size particles and dried in an oven in order to remove the absorbed moisture. Then the oven dried CSFs particles mixed with potassium bromide (KBr) in 1:100 ratio and pressed into small pellet about 1 mm thick sample used to record the FTIR spectrum under standard conditions.

RESULTS AND DISCUSSION

Chemical analysis of modified CSFs

The constituents of raw and chemically modified CSFs are exhibited in Table 1. The raw and different chemically modified CSFs were identified with the following order of cellulose content: raw CSFs(53.86) < ACSFs(57.21) < ZCSFs(61.37) < PCSFs(65.19) < SCSFs (67.41) < BCSFs (69.14). The

Table 1. Chemical constituents of raw and chemically treated CSFs

Fiber	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt %)	Wax (wt %)	Moisture (wt %)	Ash (wt %)	Density (g/cm^3)	Reference
Raw	53.86	11.43	16.97	0.59	9.93	7.22	1.2726	[16]
Optimal ACSFs	57.21	9.10	13.60	0.23	6.74	11.36	1.2930	[10]
ZCSFs	61.37	6.67	12.32	0.19	6.25	13.20	1.3270	---
PCSFs	65.19	5.21	10.11	0.14	5.58	13.77	1.3410	---
SCSFs	67.41	3.79	8.58	0.10	4.39	15.73	1.3563	---
BCSFs	69.14	3.16	7.62	0.08	4.03	15.97	1.3742	---

enhanced cellulose content and reduced hemicelluloses, lignin and wax contents and increased moisture resistance capacities in all the treated CSFs reported that there is increase in tendency of more packed crystalline order. Elimination of hemicellulose and lignin elevate the proportionate cellulose contents in the chemically modified fibers ^[18]. The raw CSFs which has less density than all other modified CSFs, and increase in density values for the modified CSFs may be due to the grafted

molecules filled all the pores and densification of fiber walls as the elimination of impurities like wax and fats [14]. It can be concluded that benzylation and stearamation are more reactive in eliminating hemicelluloses and lignin contents compared to other chemical treatments.

Thermal analysis of alkali treated GAFs

The variations of thermogravimetric analysis of chemically modified and raw CSFs are shown in TG and DTG curves (figure 1 (a) and (b)). As expected, two stages of degradation were occurred in all the modified and raw CSFs. At the beginning, the degradation is observed between 32°C and 100°C, because of moisture evaporation from the fiber. The next degradation was carried out among 210°C to 400°C which associates the degradation of hemicelluloses, cellulose and lignin. The greater decomposition temperatures impart higher thermal stability to fibers [18]. The different predominant peaks for various chemically modified CSFs are shown in the DTG curves, which represents the thermal stability of the modified CSFs. The different peaks at 317.6°C, 332.8°C, 334.5°C, 338.4°C, 342.1°C and 354.2°C represent the depolymerization of cellulose with associated weight losses of raw CSFs (33.44 %), alkali treated CSFs (35.26%), ZCSFs (36.29%), PCSFs (38.35%), SCSFs (44.07%) and BCSFs (48.04%) respectively.

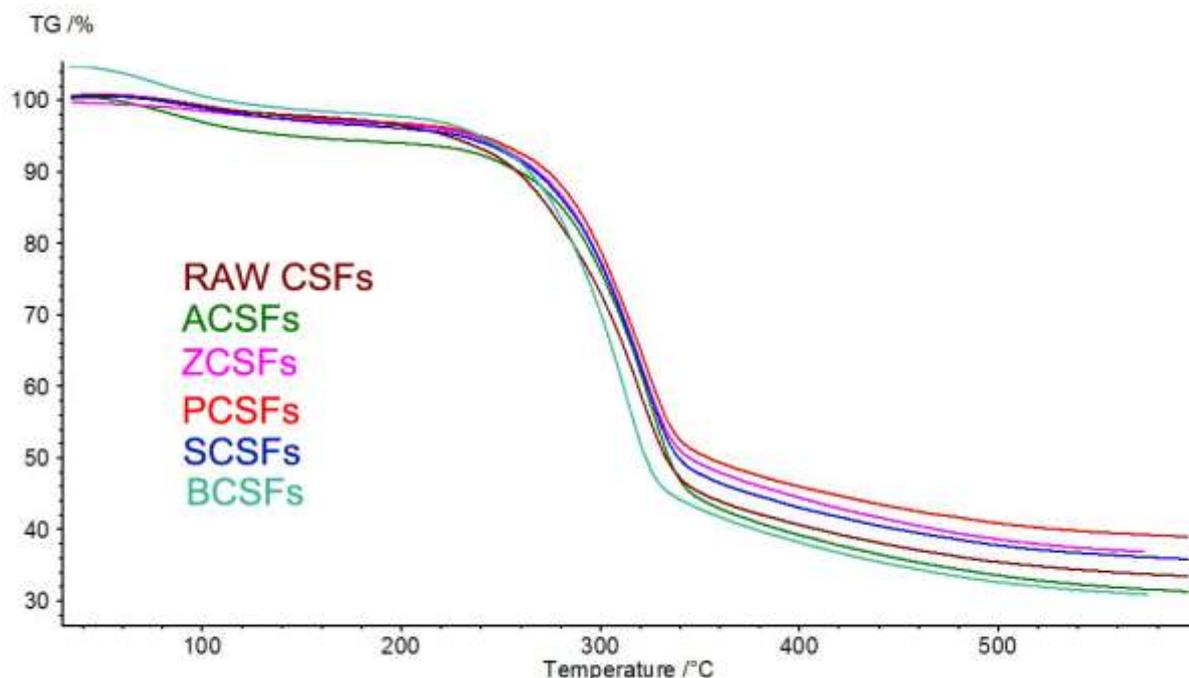


Fig.1. (a) TG curves of raw and chemically modified CSFs

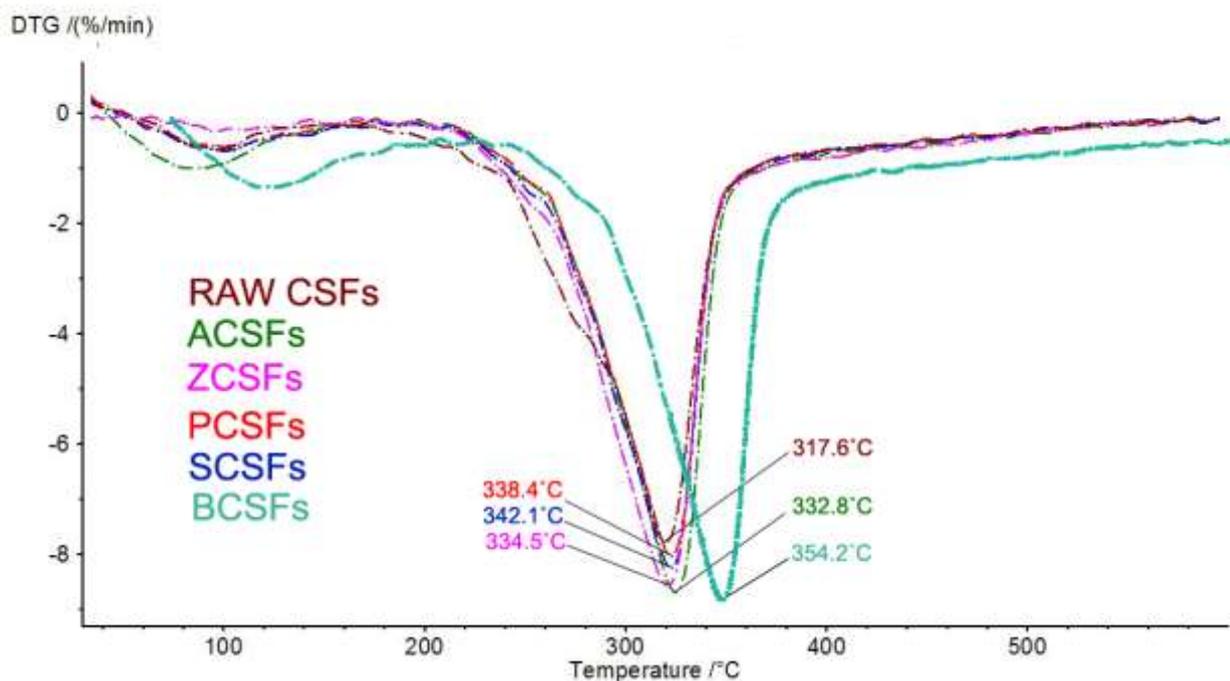


Fig.1 (b) DTG curves of raw and chemically modified CSFs

The thermal stability of chemically modified CSFs were in the following order; BCSFs (11.5%)>SCSFs (7.7%)>PCSFs (6.6%) > ZCSFs (5.32%) ACSFs (4.8%) when compared to raw CSFs, which might be due to diminishing of amorphous contents and rearrangement of structural order. The hemicelluloses decomposition starts at lower temperatures in comparison with cellulose and lignin. Normally, the degradation of lignin was carried out during broader temperature range of 210°C to 500°C [14, 18]. Moreover, in the chemically treated CSFs the residual mass around 600°C was appreciably higher than the raw CSFs. Finally, it is concluded that chemically modified CSFs have enough potential to be used as reinforcement in polymer matrices whose normal processing temperature is below 250 °C.

XRD analysis

In Figure 2, the X-Ray diffractograms were used to analyse the crystallinity of the treated CSFs. The important crystalline peak for different modified CSFs raised at $2\theta = 22.77^\circ$, and noticeable peaks appeared at $2\theta = 15.22^\circ$ and 16.44° represents the existence of cellulose - I. The cellulose is the important structural component which gives more strength and firmness to the plant cell partition walls

and fibers [21]. The CI values for the raw and different chemically modified CSFs were calculated by using the equation (1), arranged in the increasing order as follows; raw CSFs (48.96%) < ACSFs (63%) < ZCSFs (66.82%) < PCSFs (75.58%) < SCSFs (77.16%) < BCSFs (79.42%). Obviously, this confirms the following; rearrangement of crystalline structure with the accumulation of most crystalline natured regions, and appreciable elimination of hemicelluloses and other amorphous contents which will improve the proportionate crystalline cellulose contents. Finally the results conclude that chemical treatments dissolve certain portion of hemicellulose and lignin components from the fibers [18]. By removing cementing materials, the chemical modification treatments brought the increase in percentage of crystallinity index and also ends with closure and compact packing of cellulose chains [23].

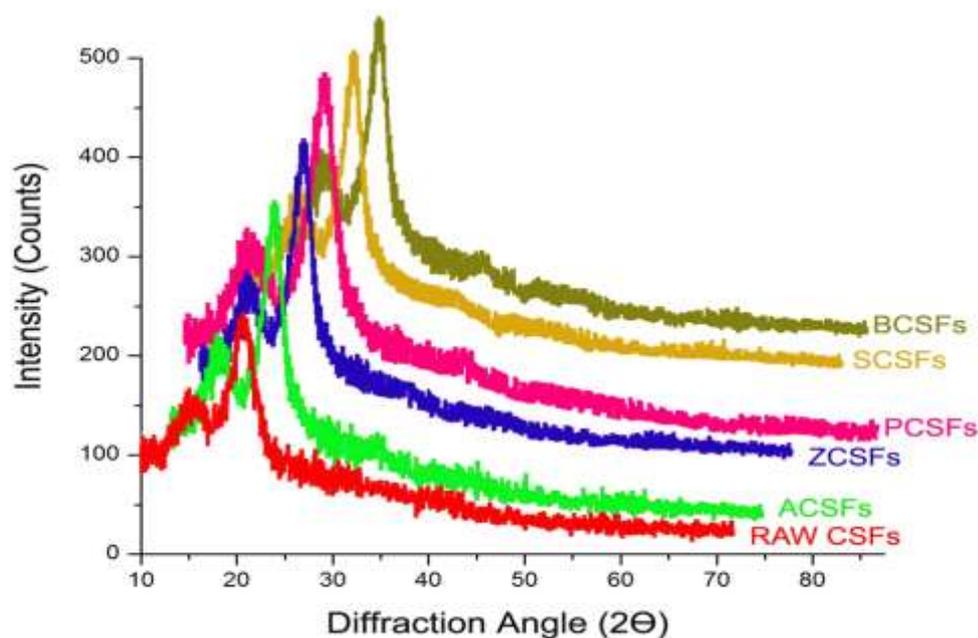


Fig.2. XRD pattern of raw and chemically modifiedCSFs

FTIR analysis

The FTIR spectra for raw and all chemically modified CSFs are exhibited in figure 3. The FTIR spectrum of raw CSFs shows the different bands of chemical groups characteristics of lignocellulosic fiber compounds such as cellulose, hemicelluloses and lignin, as resulted in [10]. The broad peak in the region $3600 - 3100 \text{ cm}^{-1}$ corresponds to the characteristic O-H stretching vibration and hydrogen bond of hydroxyl groups. Another peak observed at 1331 cm^{-1} due to alcohol group of cellulose OH

deformation was reduced in all chemically treated spectra [17, 20]. The noticeable peak at 1738 cm^{-1} corresponds to the carbonyl C=O functional groups of hemicelluloses present in raw CSFs spectrum and which is disappeared in all other chemically modified CSFs spectra. A small peak observed at 1512 cm^{-1} is associated to C=C stretching of aromatic ring of Lignin. The absorption peak identified at 897 cm^{-1} represents the existence of the β -glycosidic linkages between the monosaccharide units [10, 19]. The noticeable peaks in every spectrum at 2353 cm^{-1} , 1738 cm^{-1} and 1512 cm^{-1} robustly authenticate the diminution of wax, hemicelluloses and lignin contents performed by chemical modification of CSFs. The chemical treatments become the reason for the depolymerization of native cellulose and shorter crystallites are exposed [22-25].

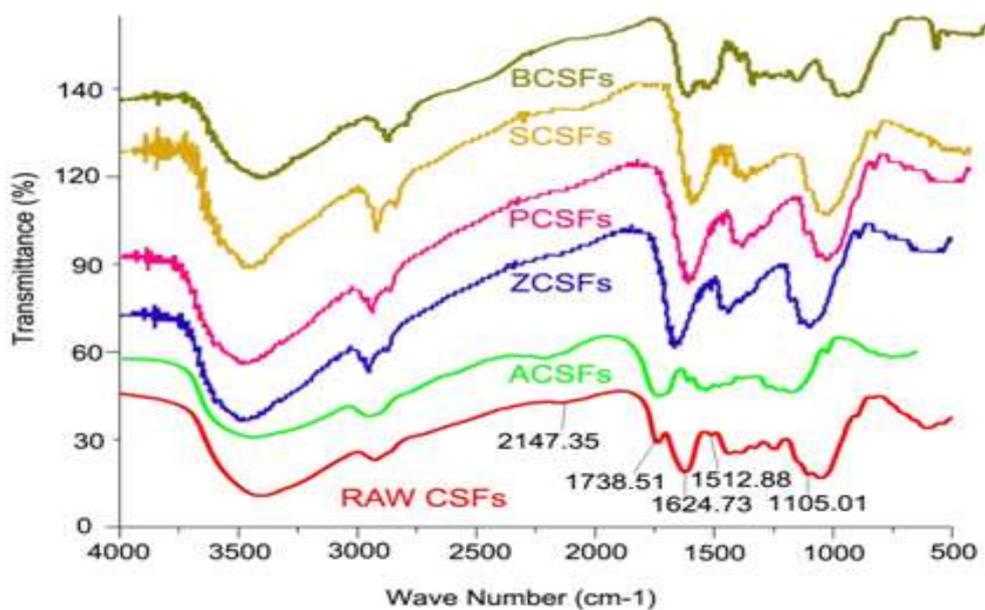


Fig.3. FTIR spectra of raw and chemically modified CSFs

CONCLUSION

In order to increase the adhesion among the fiber and matrix at the cost of degrading hydrophilicity, the CSFs were modified chemically by alkali, benzoyl chloride, potassium permanganate, stearic acid and zinc chloride treatment. The enhancement of CI values, increase in thermal stability and elimination of amorphous and wax contents prove that the physicochemical properties of CSFs were improved by various effective chemical treatments. It is clear that BCSFs have dominating physicochemical properties in comparison to other treatments. Better to conclude that CSFs are the good candidates and have enough capacity to reinforce with polymer composite matrices.

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