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Pyrolysis Process of Microwave-Enhanced Recovery of Sucker Rod Carbon Fiber Composite

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ABSTRACT

This paper recycles and reuses sucker rod carbon fiber composite by microwave technique. The high temperature dielectric parameters of sucker rod carbon fiber composite were tested with the perturbation technique of cylindrical resonator. The structure and performance of the recovered carbon fiber samples were characterized by testing methods like scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and X-ray diffractometer (XRD). The results show that: the carbon fiber of sucker rod is good at absorbing microwaves. During microwave pyrolysis, the heating rate can reach 359.46 (°C/min), which greatly shortens the processing time. In addition, the microwave technique does not affect chemical bonds and functional group types, and the resulting recycled carbon fibers can be recycled well.

1. INTRODUCTION

Carbon fiber composite is mainly prepared with resin as the matrix, and carbon fibers as the reinforcing material. In some application scenarios, the metal and ceramic are also adopted as matrices, and combined with carbon fibers, which boast excellent mechanical properties. The combination blesses the composite a series of excellent performance: high specific strength, high specific modulus, and strong corrosion resistance. The resulting new composite has been widely applied in the aerospace, automaking, and sports equipment manufacturing. In particular, the consumption of the new composite in aerospace and automaking surpasses that of carbon fiber composite by more than 50% [1].

In recent years, the sucker rod carbon fiber composite was favored in oil field operations, because it overcomes the defects of conventional steel sucker rod: large mass, intermittent operations, as well as the partial wear and piston effect in long-term operation. Numerous field applications show that the sucker rod carbon fiber composite is a lightweight material capable of withstanding high temperature, corrosion, and fatigue, as well as reducing energy consumption, and improving economic benefit [2-4].

While improving the work efficiency and standard of living, the sucker rod carbon fiber composite poses threats to the environment. During the preparation, 30-50% of the carbon fiber composite is wasted [5]. Normally, the waste of the carbon fiber composite is crushed to serve as fillers, or directly incinerated for landfill treatment. However, the high temperature- and corrosion-resistant waste cannot be easily decomposed by microorganisms underground, resulting in a high level of pollution to the surrounding soil and water sources [6]. The conventional disposal methods also greatly weaken the use value of carbon fibers, and should not be adopted to treat the waste of carbon fiber composite in the long run.

As an electromagnetic wave, the microwave can penetrate the object, and convert energy inside the materials. Compared with conventional heating, the microwave shortens the heating time, consumes less energy, and saves lots of costs [7]. Microwave pyrolysis is widely adopted for preparing alternative fuels like syngas and bio-oil through biomass pyrolysis. Dominguez et al. [8] found that, under microwave heating, the coffee shell promotes the secondary decomposition of oil; the gas yield of microwave pyrolysis is higher than that of conventional heating. Fei et al. [9] carried out microwave heating of corn straw, and observed that the pyrolysis speed increased significantly with the growing microwave power. Besides, the yield of liquid product can be increased by adding 1% of coke. Fang et al. and Qing et al. [10, 11] analyzed the damage process of sludge structure under microwave. The results show that microwave pyrolysis can effectively improve sludge dehydration, and boast great advantages in heavy metal fixation and resource reuse.

In the aerobic environment, the most representative pyrolysis technique of carbon fiber composite is the fluidized bed pyrolysis proposed by Prof. Pickering at University of Nottingham. The technique burns resin in hot air, and separates it from carbon fibers. Although the carbon fibers thus separated are clean and free of carbon deposition, the carbon fibers are serious damaged [12].

This paper mainly studies the recovery of sucker rod carbon fiber composite through microwave pyrolysis. The perturbation technique of cylindrical resonator was adopted to test the high temperature dielectric parameters of sucker rod carbon fiber composite. Multiple testing methods were adopted to characterize the structure and performance of the recovered carbon fiber samples, including scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and X-ray diffractometer (XRD).

2. METHODOLOGY

2.1 Raw materials and experimental process

The sucker rod carbon fiber composite was provided by Sinopec Shengli Oilfield Company, Dongying, eastern China's Shandong Province. The reinforcing material is T300 carbon fibers and glass fibers. The epoxy resin was taken as the matrix. Before the experiments, a 2cm long sucker rod was truncated, and placed in a quartz boat. Then, the entire quartz boat was relocated into a microwave tube furnace (Figure 1). After closing the furnace door, the dry air was passed into the furnace, and then the microwave was fed into the furnace for pyrolysis. The output frequency and power of the microwave were 2.45GHz and 0-1.5kW, respectively. The pyrolysis temperature was set to 400, 450, and 500°C. The sample was taken out after each temperature was kept constant for 10 and 30min, respectively.

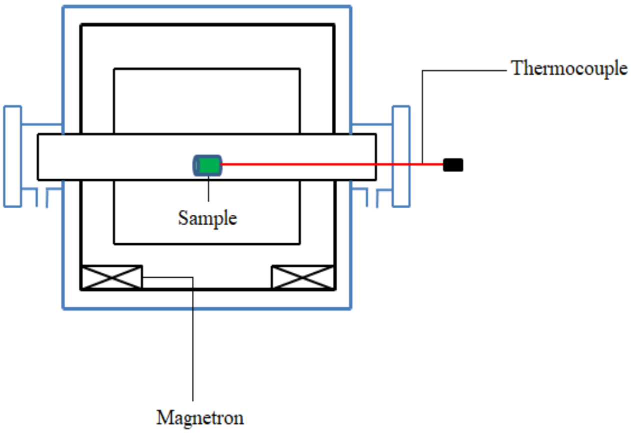

Figure 1. Schematic of microwave pyrolysis

2.2 Performance and characterization

Each sample was cut, modeled, ground, and polished. Then, the micromorphology of the recovered carbon fibers was observed under an SEM. Besides, a Fourier infrared spectrometer (IS50, Nicolet, USA) was adopted to test the absorption spectrum of the recovered carbon fibers at 400-4,000 cm^{-1}, and to characterize their functional groups. In addition, an X-ray diffractometer (XRD, Panalytical X'Pert3 Power, the Netherlands) was employed to observe the structure of the recovered carbon fibers. Finally, the dielectric properties of the sucker rod carbon fiber composite were tested by a self-designed high-temperature dielectric test system.

2.3 Equipment

Figure 1 shows the microwave tube furnace adopted in our experiments.

In our experiments, the high temperature dielectric parameter test was measured by the perturbation technique of cylindrical resonator, under the microwave frequency of 2,450MHz. As shown in Figure 2, the test system mainly includes a vector network analyzer, a water cooler, a temperature controller, a heater, a resonance cavity, a computer, an air pump, etc. During the dielectric parameter test, the quality factor and resonance frequency of the resonance cavity were tested by the vector network analyzer. Next, a quartz tube containing the sample was fed into the middle of the graphite sleeve by a pneumatic device, and heated to the test temperature by the induction heater. After that, the sample was quickly moved into the resonant cavity by the pneumatic device. Then, the vector network analyzer was adopted to measure the quality factor and resonance frequency. The test results were computed on the software in the computer, producing the dielectric parameters under different temperatures.

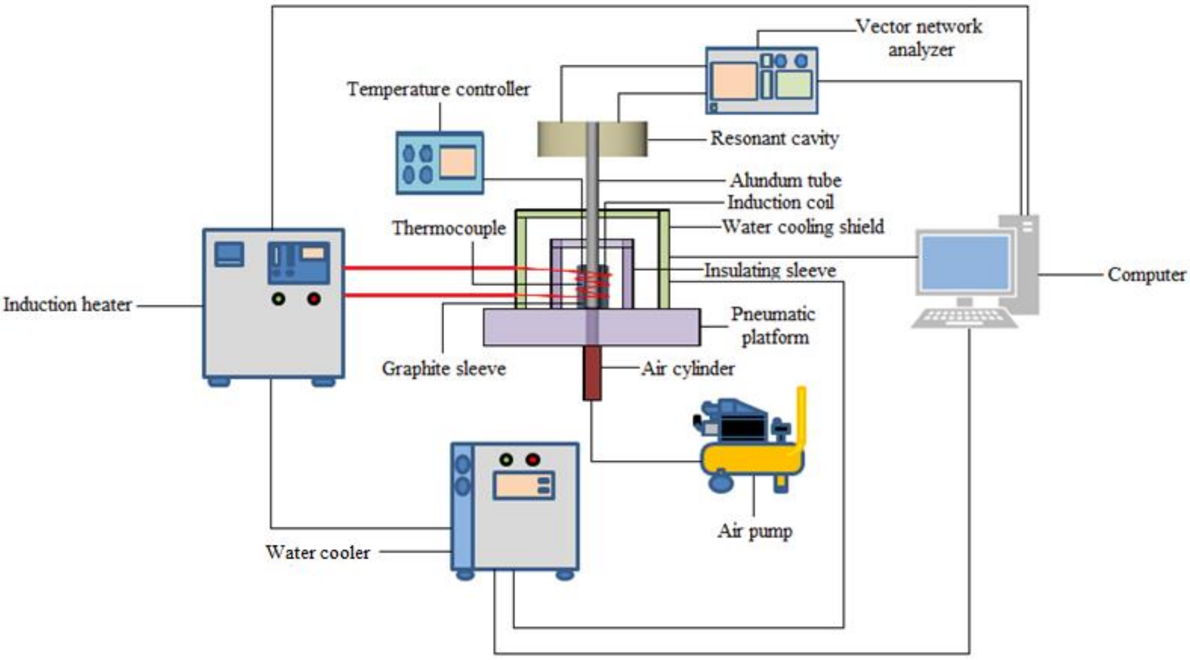

Figure 2. High temperature dielectric parameter test system

3. RESULTS AND DISCUSSION

3.1 Determination of dielectric parameters of sucker rod powder

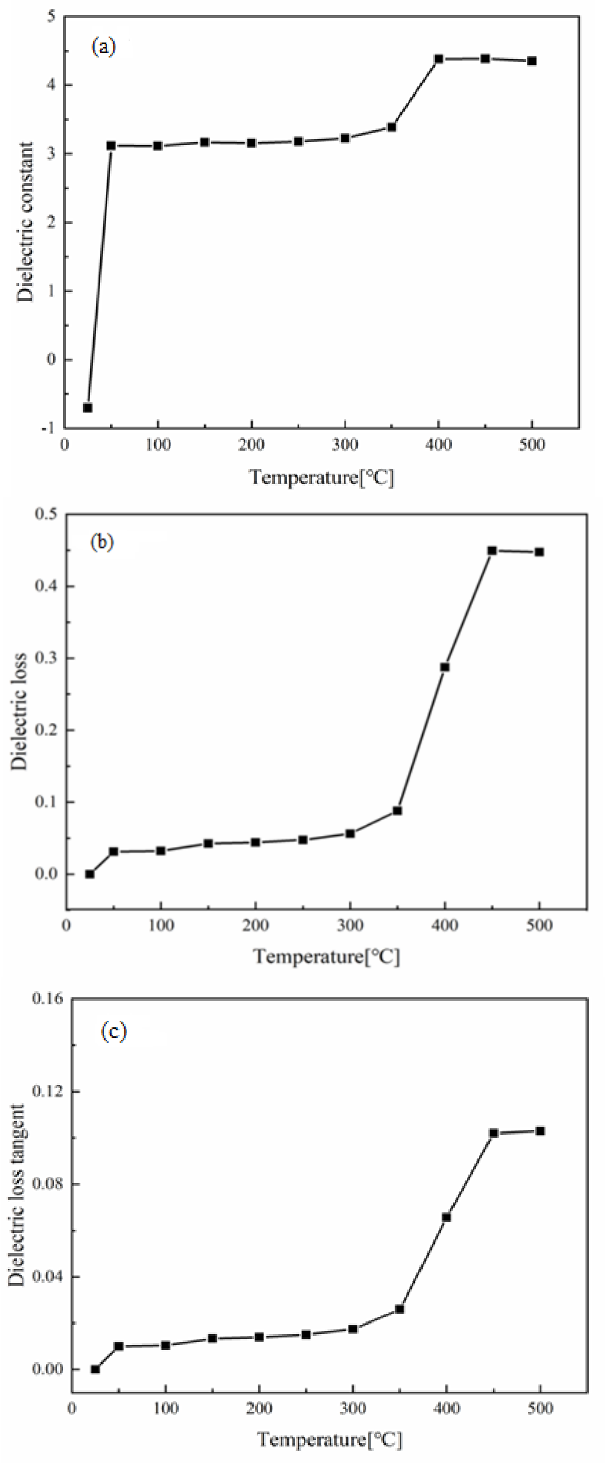

Figure 3. Variation of the dielectric parameters of sucker rod powder with temperature

Under microwave heating, the microwave interacts with the molecules of the material. The heat effect is generated by the dielectric losses. The carbon fibers contain lots of delocalized π electrons, and polarized functional groups. When the microwave acts on the sucker rod material, the polarization effect may be generated, especially on the dipole, which plays a crucial role in heating the material. The dielectric properties of the material determine the ability of the material to absorb microwave, and interact with microwave. The microwave absorption ability of the material can be mainly characterized by the dielectric constant. The greater the constant, the larger the microwave absorptivity of the material. The dielectric loss indicates the ability of the material to convert the microwave energy into thermal energy. The tangent of dielectric loss angle depicts the efficiency of the material converting the absorbed microwave energy into thermal energy.

As shown in Figure 3, when the temperature changed from the normal level to 500°C, the equivalent dielectric constant of the sucker rod increased, and the dielectric loss and the tangent of the dielectric loss angle were on the rise. This means the rising temperature enhances the material’s ability to absorb microwave, and convert the microwave energy to thermal energy. However, a negative dielectric constant was observed under normal temperature. The negative dielectric constant mainly comes from the intrinsic properties of the material. Depending on the low-frequency plasma of free electrons in the conductive carbon network, the carbon fibers in the sucker rod boast excellent conductive properties and tensile strength, and are often filled into ceramics as the conductive phase, forming a three-dimensional (3D) conductive network [13, 14]. When the external electric field frequency is lower than the plasma frequency of free electrons, a negative dielectric behavior will appear [15, 16].

3.2 Microwave heating properties of sucker rod

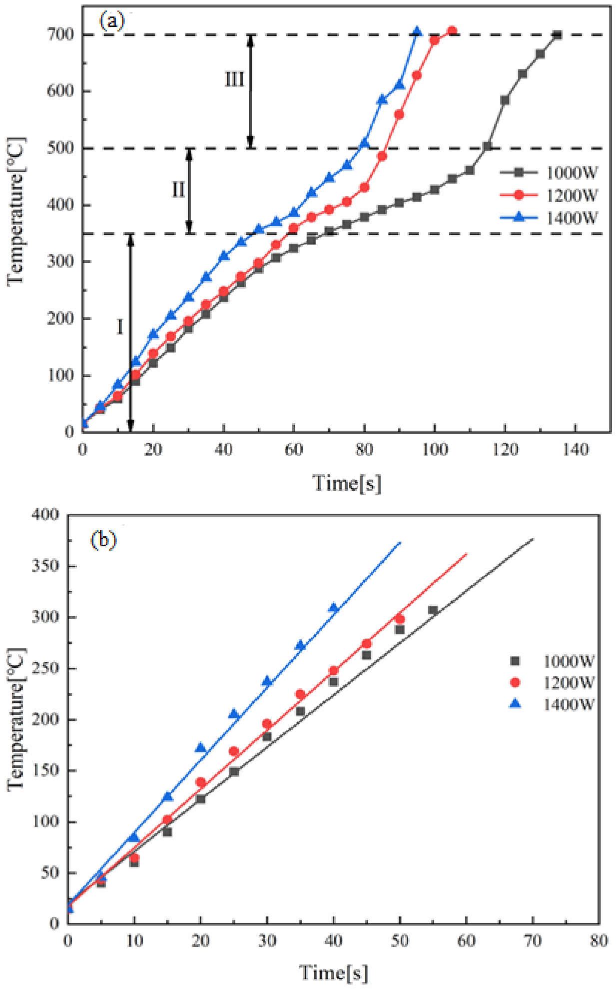

Figure 4. Variation of sucker rod temperature with microwave heating time

Figure 4 compares the heating properties of the 15g sucker rod under different microwave powers. As shown in Figure 4(a), the heating rate increased with the microwave power. The heating process can be roughly divided into three phases: rapid heating (I, III), and slow heating (II). Phase I is the softening process of the oil rod. According to Figure 4(b), during Phase I, the slope of the heating curve was 305.53(℃/min) at the microwave power of 1,000W, 344.31(℃/min) at 1,200W, and 425.24(℃/min) at 1,400W. The results demonstrate a good ability for the sucker rod to absorb microwave. Hence, the sucker rod has a good heating performance. The slowdown of heating rate in Phase II is probably because the resin softening needs to absorb lots of heat to decompose the fibers. The results in Figure 4 agree well with the test data in Figure 3, laying the basis for experiments on recovering sucker rod carbon fibers through microwave pyrolysis. In Phase III, the rising heating rate is possible associated with the exothermic reaction of carbon fibers. The wave absorbing performance of the carbon fiber composite mainly depends on the components and structure of the material. The sucker rod is a sandwich of glass fibers and carbon fibers. The outermost glass fibers are highly transmissive. As a resistive absorbing material, the carbon fibers have a small resistivity. Under an external magnetic field, the carbon fibers would resonant with the incident electromagnetic wave, forming a dispersion current. The current will attenuate in the surrounding matrix. In this process, the electromagnetic wave energy is transformed into thermal energy and other forms of energy [17-19].

3.3 Micromorphology of recycled carbon fibers

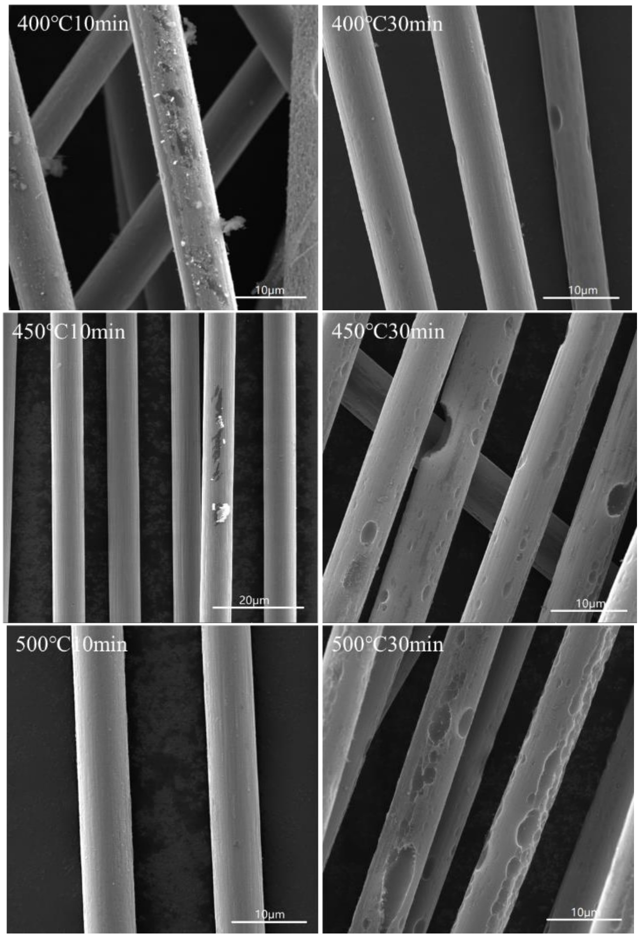

Figure 5. Micromorphology of recycled carbon fibers

Figure 5 shows the micromorphology of recycled carbon fibers recovered through microwave pyrolysis under different conditions. When the heating temperature was 400°C, lots of resin were left on the recycled carbon fibers after the temperature was held for 10min. Fewer particles were observed, and pits were found on the carbon fibers, after the temperature was held for 30min. This means the carbon fibers are partly oxidized under long-term heating. When the heating temperature was 450°C, a few resins were attached on the recycled carbon fibers after the temperature was held for 10min. Many pits and defects of different degrees were detected on the carbon fibers, after the temperature was held for 30min. When the heating temperature was 500°C, the recycled carbon fibers obtained after 10min of temperature holding were smoother than those obtained at the heating temperatures of 400°C or 450°C, with virtually no residual substance on the surface. The carbon fibers obtained after 30min of temperature holding were seriously oxidized on the surface, and their surface structure was damaged.

3.4 Infrared spectrum analysis of recycled carbon fibers

Figure 6 shows the main functional groups of the virgin and recycled carbon fibers in the Fourier infrared spectra. The peaks at $2,350cm^{-1}$, $1,630cm^{-1}$, $1,380cm^{-1}$, and $1,040cm^{-1}$ are attributable to the tensile vibration of C≡N, the stretching vibration of the C=C of the aromatic ring skeleton, the stretching vibration of the C-H of methyl, and the stretching vibration of the C-O of ether, respectively. Under the same temperature holding time, with the rise of temperature, C=C gradually weakened to approach the strength of the virgin carbon fibers. A possible reason is that carbon is generated on the carbon fibers during low temperature pyrolysis. Compared with those under the two conditions of 400°C and 450°C, the carbon fibers recycled after being held at 500°C in the air atmosphere and the virgin carbon fibers were not very different in the absorption peak intensity of each functional group, and were basically the same in terms of chemical bonds. Thus, the heating condition does not change the chemical structure of the recycled carbon fibers.

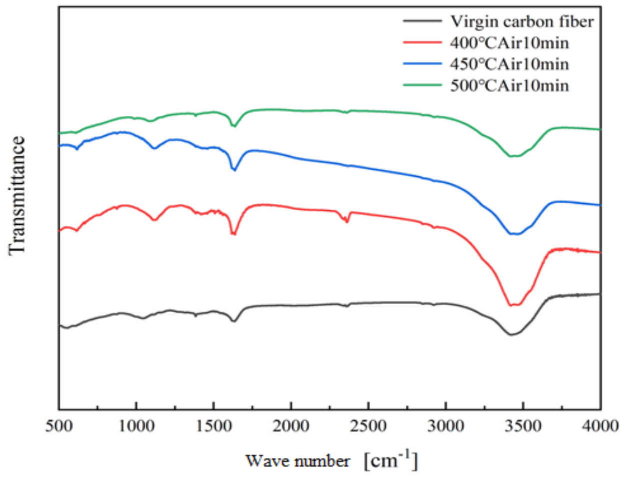

Figure 6. Infrared spectra of virgin carbon fibers and recycled carbon fibers

3.5 XRD analysis of recycled carbon fibers

Figure 7 displays the XRD spectra of virgin carbon fibers, and those of the carbon fibers recycled after being held for 10min under 400℃, 450℃, and 500℃ in the air atmosphere. In the XRD spectra, 2θ=25° represents the diffraction characteristic peak on the (002) plane. The peak is related to the graphitized structure in the fibers [20]. The crystalline parameters of the carbon fibers were computed by the Bragg's Law and the Debye Scherrer equation (Table 1). For virgin carbon fibers, the grain size and the interlamellar spacing of (002) plane were 15.0563nm, and 0.3477nm, respectively. As the temperature increased, the grain size of the recycled carbon fibers gradually decreased, which may be attributed to the weakening of graphitization under carbon oxidation. The characteristic peaks of the carbon fibers recycled at 400℃ and 450℃ were relatively weak, a sign of incomplete graphitized structure. Sauder et al. [21] noted that the increase of interlamellar spacing will reduce the tensile modulus. Hence, the carbon fibers recycled after being held for 10min at 500℃ in the air atmosphere have a lower tensile modulus than the virtual carbon fibers.

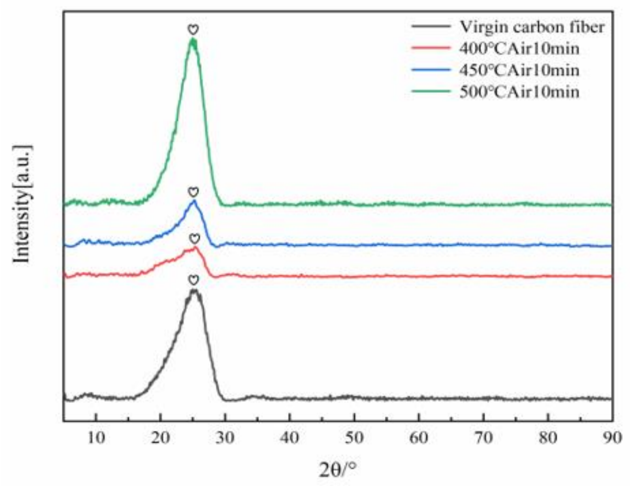

Figure 7. XRD spectra of virgin carbon fibers and recycled carbon fibers

Table 1. Crystalline parameters of virgin carbon fibers and recycled carbon fibers

Sample	2-Theta	FWHM	d_{002}/nm	D/nm
Virgin carbon fibers	25.598	0.535	0.347706794	15.05629599
400Air10min	25.422	0.361	0.350073983	22.30559075
450Air10min	25.316	0.4436	0.351515694	18.46477509
500Air10min	25.052	0.754	0.355159854	10.67175053

4. CONCLUSIONS

The following conclusions were drawn through the above analysis: The sucker rod carbon fiber composite is good at absorbing the microwave. Its dielectric constant gradually increases with the growing temperature. During microwave pyrolysis, the heating rate can reach 359.46 (℃/min), which significantly enhances the pyrolysis efficiency, and shortens the processing time. In the air atmosphere, the carbon fibers recycled from the sucker rod carbon fiber composite after being held for 10min at 500℃ have a slightly lower graphitization degree and tensile modulus than the virgin carbon fibers, but the same types of chemical bonds, and similar absorption peak intensities. Hence, the carbon fibers obtained under that condition can be effectively recycled.

REFERENCES

[1] Holmes, M. (2014). Global carbon fibre market remains on upward trend. Reinforced Plastics, 58(6): 38-45. https://doi.org/10.1016/S0034-3617(14)70251-6

[2] Hensley, H.N., Tanner, C.J. (1984). Graphite composite tape in beam-pumped oil wells. In SPE Annual Technical Conference and Exhibition. OnePetro, spe13200. https://doi.org/10.2118/13200-MS

[3] Tanner, C.J., Bender, R.E., Simson, A.K., McCutchen Jr, H. (1986). Ribbon rod for use in oil well apparatus, US, 4563391.

[4] Foley, W.L., Hensley, H.N. (1996). Ribbon rod-improvement in sucker rod technology shows need to re-evaluate current artificial lift installations. In SPE Western Regional Meeting. OnePetro, 573. https://doi.org/10.2118/35708-MS

[5] Pickering, S.J. (2006). Recycling technologies for thermoset composite materials-current status. Composites Part A: Applied Science and Manufacturing, 37(8): 1206-1215. https://doi.org/10.1016/j.compositesa.2005.05.030

[6] Rybicka, J., Tiwari, A., Leeke, G.A. (2016). Technology readiness level assessment of composites recycling technologies. Journal of Cleaner Production, 112: 1001-1012. https://doi.org/10.1016/j.jclepro.2015.08.104

[7] Chandrasekaran, S., Ramanathan, S., Basak, T. (2012). Microwave material processing-a review. AIChE Journal, 58(2): 330-363. https://doi.org/10.1002/aic.12766

[8] Dominguez, A., Menéndez, J.A., Fernandez, Y., Pis, J.J., Nabais, J.V., Carrott, P.J.M., Carrott, M.R. (2007). Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas. Journal of Analytical and Applied Pyrolysis, 79(1-2): 128-135. https://doi.org/10.1016/j.jaap.2006.08.003

[9] Fei, Y., Ruan, R., Deng, S. (2006). Microwave Pyrolysis of Biomass. Portland, Oregon.

[10] Fang, L., Tian, Y., Wu, W.N., Cao, C.Y. (2008). Characteristic study of the solid, liquid and gas produced by microwave pyrolysis of sewage sludge. Journal of Safety and Environment, 8(1): 5. https://doi.org/10.3969/j.issn.1009-6094.2008.01.009

[11] Qing, W., Huan, X.K., Liu, H.P., Sun, B.Z., Jia, C.X. (2008). Microwave induced pyrolysis of Huadian oil shale. Journal of Chemical Industry and Engineering (China), 59(5): 6. https://doi.org/10.3321/j.issn:0438-1157.2008.05.034

[12] Pickering, S.J., Kelly, R.M., Kennerley, J.R., Rudd, C.D., Fenwick, N.J. (2000). A fluidised-bed process for the recovery of glass fibres from scrap thermoset composites. Composites Science and Technology, 60(4): 509-523. https://doi.org/10.1016/S0266-3538(99)00154-2

[13] Tsutaoka, T., Massango, H., Kasagi, T., Yamamoto, S., Hatakeyama, K. (2016). Double negative electromagnetic properties of percolated Fe53Ni47/Cu granular composites. Applied Physics Letters, 108(19): 191904. https://doi.org/10.1063/1.4949560

[14] Tsutaoka, T., Kasagi, T., Yamamoto, S., Hatakeyama, K. (2013). Low frequency plasmonic state and negative permittivity spectra of coagulated Cu granular composite materials in the percolation threshold.

Applied Physics Letters, 102(18): 181904. https://doi.org/10.1063/1.4804379

[15] Shi, Z.C., Fan, R.H., Zhang, Z.D., Qian, L., Gao, M., Zhang, M., Yin, L.W. (2012). Random composites of nickel networks supported by porous alumina toward double negative materials. Advanced Materials, 24(17): 2349-2352. https://doi.org/10.1002/adma.201200157

[16] Shi, Z.C., Fan, R.H., Yan, K.L., Sun, K., Zhang, M., Wang, C.G., Zhang, X.H. (2013). Preparation of iron networks hosted in porous alumina with tunable negative permittivity and permeability. Advanced Functional Materials, 23(33): 4123-4132. https://doi.org/10.1002/adfm.201202895

[17] Vinoy, K.J., Jha, R.M. (1995). Trends in radar absorbing materials technology. Sadhana, 20(5): 815-850. https://doi.org/10.1007/BF02744411

[18] Cai, H.S. (2019). Study on electromagnetic properties of fiber reinforced epoxy resin absorbing composites. Nanjing University of Aeronautics and Astronautics, 2019.

[19] Shang, K., Wu, Z.H., Zhang, L.P., Wang, Q., Zhegn, H.K. (2019). Research progress of fiber absorbing material. New Chemical Materials, 47(9): 24-27.

[20] Qian, X., Zhi, J., Chen, L., Zhong, J., Wang, X., Zhang, Y., Song, S. (2018). Evolution of microstructure and electrical property in the conversion of high strength carbon fiber to high modulus and ultrahigh modulus carbon fiber. Composites Part A: Applied Science and Manufacturing, 112: 111-118. https://doi.org/10.1016/j.compositesa.2018.05.030

[21] Sauder, C., Lamon, J., Pailler, R. (2004). The tensile behavior of carbon fibers at high temperatures up to 2400 C. Carbon, 42(4): 715-725. https://doi.org/10.1016/j.carbon.2003.11.020