Carbon Fiber Heat Treatment Temperature and Electrophysical Properties of Composite Materials Filled with These Fibers

S. V. LETYAGIN, V. G. SHEVCHENKO, A. T. PONOMARENKO, and V. N. KESTELMAN*,†

Institute of Synthetic Polymeric Materials, Russian Academy of Science, 117393 Moscow, Profsoyuznaya, 70, Russia

SYNOPSIS

Conductivities of composites filled with different carbon fibers having different heat treatment temperatures (HTT) have been studied. It is shown that conductivity realization coefficient decreases with the increase of HTT. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The increase of realization coefficients of components in composite materials (CM), especially conducting (CCM), is becoming a high-priority task. Designing a CCM is usually carried out by changing the concentration of functional fillers.[1,2] At the same time another method is equally reasonable, that is, preliminary modification of fillers allowing one to control the properties of CCM over a wide range at the same filler concentration.

The aim of this work was to elucidate the structure of CCMs containing short carbon fibers (CF) having different HTT in the range 750–2200°C and to study their electrophysical properties.

EXPERIMENTAL

Conductivity was studied on CF plastics made from phenolformaldehyde resin LBS-1 and CF having different HTT, commercially available in Russia. Two types of hydrated cellulose-based fibers have been used: Uglen and UVK. They differ in the composition of precursor fibers and the conditions of heat treatment. Specimens were made in two steps: preparation of prepregs and their pressure molding. The first step included cutting the fibers to the length of 10 mm, impregnating with resin, and drying. Prepregs were pressure molded in a 120 × 15 × 10 mm mold at 160°C and pressure 32–35 MPa for 20 min. Filler concentration in CM was maintained at 60 wt %.

Conductivity was measured by a modified four-probe method[3] along the sample (σ_1), in the width direction (σ_2), and in the thickness direction (σ_3). Mechanical properties of CM were measured according to the Russian standards.

RESULTS AND DISCUSSION

It is known that for random distribution of fibers, their packing density decreases with increasing fiber aspect ratio L/d and is not higher than 20 vol % when $L/d = 10$.[4] In CM studied in this paper $L/d \geq 100$ (accounting for sticking of fibers) and packing density should be much lower. Under these conditions packing density can be increased by a forced method only, for example, due to bending or breakage of fibers. As a result, at filler concentration of 60 wt % (ca. 54 vol %) practically all the fibers are more or less deformed, all of them nevertheless lying in the compaction plane (perpendicular to the compacting direction). In other words, packing of fibers in the compacting plane is more random than in the perpendicular direction. This is confirmed by optical observation of cuts of these materials.

The picture changes with increasing fiber length. When L exceeds the width and thickness of the

* To whom correspondence should be addressed.
† Present address: International Trading Partners Ltd., Suite 210, 259 Radnor Chester Road, Radnor, Pennsylvania 19087

Journal of Applied Polymer Science, Vol. 50, 2035–2038 (1993)
 CCC 0021-8995/93/112035-04

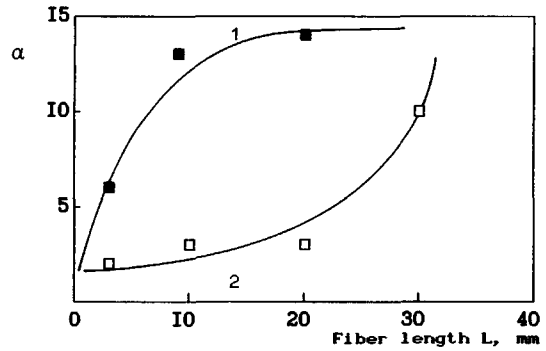

Figure 1 Anisotropy coefficients α_3 and α_2 (definitions see text) versus fiber length $L(v_f = 0.54)$.

sample, the fibers also become oriented in the compaction plane.

This can be seen from Figure 1, which shows the dependencies of $\alpha_3 = \sigma_1/\sigma_3$ and $\alpha_2 = \sigma_1/\sigma_2$ on the fiber length. The values α_3 and α_2 qualitatively reflect fiber orientation in vertical and horizontal planes, respectively. With increasing L, α_3 and α_2 curves converge, i.e., packing tends to become singly oriented. So, the composites of interest are intermediate between truly chaotic and single oriented fiber materials differing from them in the coefficients of fiber properties realization.

Figure 2 presents the dependence of fiber conductivity in two directions, 1 and 3 on Uglen fiber volume fraction (fiber HTT 900°C). It is interesting to observe the behavior of anisotropy $\alpha_3 = \sigma_1/\sigma_3$ presented in Figure 3. The presence of the maximum on this curve is clearly the result of different fiber packing, as described above.

In calculations of electrical, thermal, and mechanical properties of composite materials, starting from the constituents properties, it is common to use the rule of mixture. This approach can also be applied to the conductivity of carbon fiber composites[5]:

$$\sigma_c = v_f \sigma_f + (1 - v_f)\sigma_m$$

where σ_c, σ_f, σ_m are conductivities of CM, fiber, and the matrix, respectively; v_f is the fiber volume fraction in CM. The second term in this equation in case of insulating matrix can be neglected. The exact equality $\sigma_c = v_f \sigma_f$ is valid only for longitudinal conductivity in oriented or defect free carbon fiber plastics, or materials in which defects are effectively healed due to low contact resistance between the fibers. In other cases this equation will not hold. If we introduce a dimensionless coefficient K_r: $\sigma_c = K_r v_f \sigma_f$, we can estimate from its value the realization of filler properties in conducting composite material. We call K_r the coefficient of realization of filler conductivity and define it as $K_r = \sigma_c/(v_f \sigma_f)$. K_r depends on many factors, such as fiber orientation, conductivity and surface energy, matrix prop-

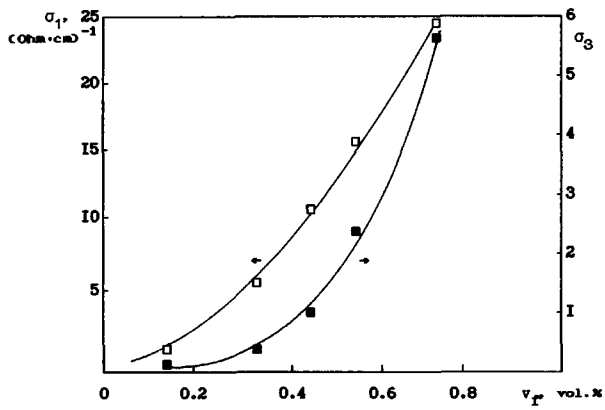

Figure 2 Conductivity of plastics based on Uglen fibers with HTT of 900°C measured in the lengthwise (σ_1) and transverse (σ_3) directions vs. fiber volume fraction.

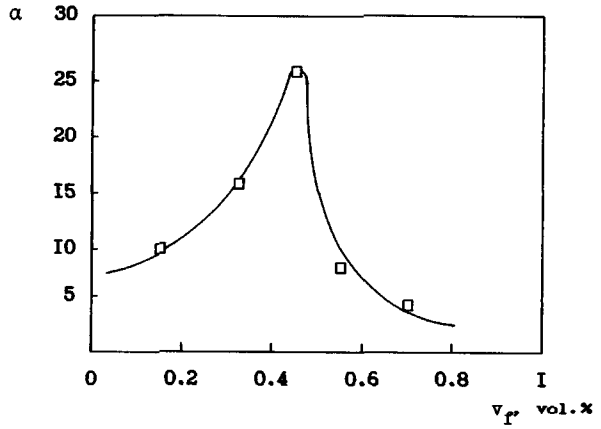

Figure 3 Anisotropy α_3 of conductivity of the plastic based on Uglen fibers with HTT of 900°C vs. fiber volume fraction.

Table I Conductivities of CF Phenoplastics Based on PAN and CL Carbon Fibers

Fiber Type	Trade Name	$\sigma_1 \times 10^2$ $(\Omega \cdot \text{cm})^{-1}$
PAN	LU-2	106
PAN	Ellur	40
PAN	Culon	100
CL	Ural N-24	56
CL	Ural LO	83

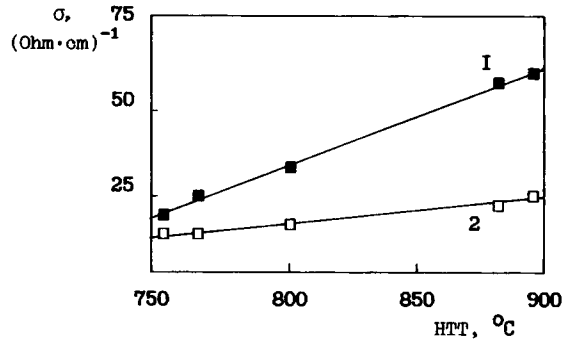

Figure 4 Dependence of (1) Uglen fibers and (2) Uglen-based plastic conductivities on fiber HTT ($v_f = 0.54$).

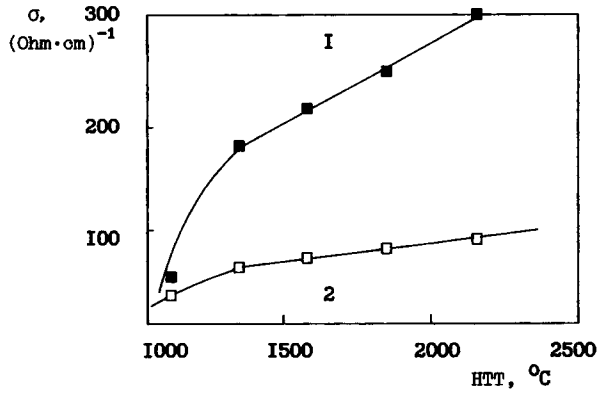

Figure 5 Dependence of (1) UVK fibers and (2) UVK-based plastic conductivities on fiber HTT ($v_f = 0.54$).

erties and, finally, on the ratio between specimen dimensions and mean defectless length in the fiber.

The above reasoning seems to be confirmed by the following model experiment on conductivities of carbon fiber tow (with 5000 monofilaments) and separate monofilaments. Within 5%, their values of σ_f are equal. After impregnating with a viscous wetting liquid, fiber σ_f is unchanged, while two σ_f becomes 25% higher. After washing out the liquid with a solvent, tow σ_f returns to the initial value. This experiment shows that bad contacts between the fibers (some of them can be broken) increase composite conductivity, accordingly the value of K_r is reduced.

It is evident that disorientation and decrease of mean fiber length lower K_r still more, with contact resistance between the fibers being important in these effects.

As was shown earlier,[6] method of preparation and σ_f of initial fibers barely influence composite conductivity. Table I presents the data on lengthwise conductivity of LBS-1-based CF plastics made of polyacrylonitrile (PAN) and cellulose (CL) fibers, having σ_f in the range 10^2–10^3 $(\Omega \cdot \text{cm})^{-1}$.

To explain this experimental fact, we investigated the tensor of conductivity in unidirectionally reinforced phenoplastics made with CF of Uglen and UVK types as a function of HTT. It is known that increasing HTT from 600 to 2000°C sharply changes practically every fiber characteristic, surface energy changing much less than conductivity.[7] For this reason a series of CF plastics with fibers having different HTT is the optimal subject for studying the dependence of composite conductivity on CF σ_f, since under these conditions all other properties that influence the contact conductivity change minimally. This series also allows one to study the dependence of K_r on fiber σ_f.

Figures 4 and 5 show the lengthwise conductivity (σ_1) of CF plastics and fibers themselves (σ_f) versus HTT of the latter.

Calculations show that with increasing HTT K_r tends to decrease from 0.85 at HTT = 750°C to 0.57 at HTT = 900°C (see Tables II and III).

As follows from Figure 3, plastic based on UVK fiber with HTT = 1200°C has an unusual property; for this material $K_r > 1$. This result is a mean value from several samples with variations not in excess of 5.5%. As preliminary investigations show, this result is a consequence of removal of impurities from the fiber surface, which act as electron traps with subsequent increase of charge carriers and conductivity of the fiber itself. This effect is observed for certain fibers with low HTT, having defective carbon structure.

It follows from Figure 3 that for all plastics but one, (UVK fiber with HTT 1200°C), K_r is between

Table II Dependence of Uglen Fibers Conductivity (σ_f), Conductivity (σ_c), and Coefficient of Realization (K_r) of Phenolic Plastics from These Fibers on Fiber HTT ($v_f = 0.54$)

HTT°C	750	760	770	800	880	900
σ_f $(\Omega \cdot \text{cm})^{-1}$	13.5	17.9	20	31.2	58.8	62.5
σ_c $(\Omega \cdot \text{cm})^{-1}$	6.2	8.2	9.6	12.2	17.5	19.2
K_r	0.85	0.85	0.88	0.72	0.55	0.57

Table III Dependence of UVK Fibers Conductivity (σ_f), Conductivity (σ_c), and Coefficient of Realization (K_r) of Phenolic Plastics from These Fibers on Fiber HTT ($v_f = 0.54$)

HTT°C	1200	1400	1600	1800	2000	2200
σ_f $(\Omega \cdot cm)^{-1}$	45.5	188.7	233	238	270	313
σ_c $(\Omega \cdot cm)^{-1}$	26.3	62.5	71.4	76.9	83.3	83.8
K_r	1.1	0.61	0.57	0.60	0.57	0.49

0.61 (HTT = 1400°C) and 0.49 (HTT = 2200°C). Comparison of this data with the results of Table I and Figure 2 shows that when σ_1 is below a critical value of $\sigma_1^* = 10^1$–10^2 $(\Omega \cdot cm)^{-1}$, K_r is high enough, gradually decreasing with σ_1 approaching this value, when K_r is about 0.6. When σ_1 becomes less than σ_1^*, K_r decreases to 0.3–0.4. The possible explanation can be that when $\sigma_f < \sigma_1^*$, resistance of a single fiber is higher than that of the contact. At the same time, when $\sigma_f > \sigma_1^*$, contact resistance prevails and decreasing σ_f does not cause any considerable decrease of composite conductivity. From this data one can evaluate contact resistance between the fibers, which turns out to be about 10^4 Ω if fiber diameter is 9 μm and the mean fiber length between the contacts is 5 mm. Unfortunately, the nature of the contact is not clear.

Some other physical properties of the plastics have also been measured. The data show that physico-mechanical properties of CM are at the same level for all fiber fillers and the possibilities of their use for any particular engineering problem should be considered separately.

CONCLUSION

The usefulness of the concept of coefficient of realization of filler conductivity in the analysis of the electric properties of composite materials has been demonstrated. It was found that, with the increase of HTT, the coefficient K_r decreases. This result allows one to estimate the value of contact resistance between individual fibers in the composite, which was found to be 10^4 Ω.

REFERENCES

1. A. T. Ponomarenko and V. G. Shevchenko, *Mendeleev Chem. J. (USSR)*, **34**, 507, (1989).
2. A. T. Ponomarenko, V. G. Shevchenko, I. A. Tchmutin, A. A. Ovchinnikov, and N. S. Enikolopyan, in *Polymer Composites*, Walter de Gruyter, Berlin-New York, 1986, p. 67.
3. A. R. Blythe, *Poly. Testing*, **4**, 195 (1984).
4. H. S. Katz and J. V. Milewski, Eds., *Handbook of Fillers and Reinforcements for Plastics*, Part 1, Van Nostrand Reinhold, New York, 1978.
5. M. O. W. Richardson, Ed., *Polymer Engineering Composites*, Appl. Sci. Publ. Ltd. London, 1977.
6. R. L. Mokienko, A. T. Ponomarenko, V. G. Schewtschenko, S. A. Dunowski, W. S. Barsukow, T. I. Krementschugskaja, W. W. Kuzygina, S. N. Piroshok, and S. W. Smetanin, *Elektrisch Aktive Polymer Kompositionen. 2 Tagung uber Polymere fur Elektrotechnik/Elektronik (Mikroelektronik)*, Vortrage, Berlin (DDR), 1985, p. 370.
7. M. R. Tarasevich, *Electrochemistry of Carbons* (in Russian), Nauka, Moscow, 1984, p. 29.

Received April 2, 1992
Accepted March 9, 1993