The effects of conditions of moulding on the surface resistivity in the range of 10^6 to 10^{10} ohms/square of a carbon-fibre/poly(ether sulphone) short-fibre composite

Carol L. Schutte* and R. Owen Hutchins
ICI Advanced Materials, 475 Creamery Way, Exton, PA 19341, USA
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The logarithm of the surface resistivity, log(*SR*), for a poly(ether sulphone)/carbon-fibre composite ranged between 6.23 and 10.66, depending on the conditions of moulding. The statistically significant variables were: the injection pressure, P_I; the temperature of the mould, T_{mould}; and the temperature of the barrel, T_{barrel}. The fibre lengths and distributions in the samples moulded under the extreme conditions for T_{mould} and P_I were not significantly different from each other—at 126 μm and median lengths at 100–110 μm. However, the lengths of the fibres at the surface of these samples, shorter than those in the centre, were slightly longer for the more conductive sample, which was moulded at maximum settings of both P_I and T_{mould}: the average fibre length was 114 ± 77 μm and median 90–100 μm for the more conductive sample, compared with 109 ± 82 μm and median 80–90 μm for the sample moulded at minimum settings of P_I and T_{mould}. The trend in relative concentration of the fibres at the surface for these samples was consistent with that in the log(*SR*); the sample with lower *SR* had a slightly higher concentration of fibres from the surface through a depth of approximately 500 μm. We propose a physical model whereby the content of fibres at the surface and their length influence the surface resistivity. Although the orientation of the fibres has the potential to influence the surface resistivity of the composites, there was no significant difference in orientation for samples examined in this study.

(Keywords: poly(ether sulphone); carbon fibre; composite; static dissipation; injection moulding; surface resistivity)

INTRODUCTION

High-temperature materials that have a controlled surface resistivity (*SR*) are useful for many applications, particularly for dissipating static charge generated from processing of integrated-circuit (IC) chips[1–7]. The desired resistivity for these applications, typically 10^5 to 10^{12} ohms/square, is in the steep part of the percolation curve[8], and is therefore difficult to achieve reproducibly. In this region, several factors control the *SR*: the content of fibres and their lengths, the conditions of processing of the composite, and possibly the conditions of moulding. Previous studies by Bailey and coworkers have focused on studies of moulding conditions, comparing long- and short-fibre composites for optimizing mechanical properties[9–12]. This study focused on the effect of the conditions of moulding of the sample on their resulting surface resistivities. The variables were: the temperature of the barrel (T_{barrel}) and the mould (T_{mould}); the injection, holding and back pressures (P_I, P_H and P_B); and the speed of the screw (S_{screw}). We measured the surface resistivities (*SR*) of the resulting plaques, calculated the standard deviations (*SD*) of their surface resistivities, and characterized selected moulded discs to develop a physical interpretation of the effect of the conditions of moulding on their surface resistivities.

EXPERIMENTAL

Materials and processing

We used one batch of a poly(ether sulphone) (PES) containing approximately 6% (w/w) carbon fibres and moulded samples into round discs (mould dimensions 1/8 inch × 3 inch (3 mm × 76 mm)) on a 75 ton Arburg moulding machine (model 221.75.350) equipped with a standard screw. The conditions of moulding are listed in *Table 1*.

Characterization

Measurements of surface and volume resistivities, typically of five discs for each condition of moulding, were performed according to ASTM-D-257 (modified to utilize voltages less than 500 V) on a Dr. Thiedig Milli-to 2 resistance meter equipped with low- and high-voltage leads, a C-clamp, variable-pressure sample holder, and surface and volume resistivity test electrodes. For the measurement of *SR*, the electrodes are placed parallel to the orientation of flow of the mould and opposite to the side with the 'knock-out' pins.

*To whom correspondence should be addressed. Current address: Room A209/Building 224, NIST, Gaithersburg, MD 20899, USA

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Table 1 Conditions for moulding study and results of surface resistivity

Study no.	T_{barrel} (°F)[a]	Pressures (psi) P_I	P_H	P_B	S_{screw}[b]	T_{mould} (°F)[a]	log(*SR*) (*SD*)
1	700	1100	700	50	30–40	250	7.93 (0.92)
2	700	1200	850	100	350	250	8.28 (0.54)
3	700	900	600	50	460	250	8.99 (0.75)
4	700	1200	850	100	30–40	250	7.55 (0.48)
5	700	850	500	50	100	350	8.20 (0.40)
6	700	1100	900	100	100	350	7.25 (0.21)
7	700	800	500	50	460	350	9.02 (0.92)
8	700	1100	800	100	460	350	6.92 (0.97)
9	750	850	550	50	150	250	7.57 (0.89)
10	750	1150	800	100	150	250	6.63 (0.23)
11	750	900	600	50	460	250	7.05 (0.38)
12	750	1150	800	100	460	250	6.60 (0.20)
13	750	850	550	50	150	350	6.65 (0.63)
14	750	1100	850	100	150	350	7.12 (0.56)
15	750	650	450	50	460	350	7.61 (0.30)
16	750	1100	800	100	460	350	6.65 (0.42)
17	725	650	450	100	100	250	8.87 (0.39)
18	725	1100	450	100	100	250	7.12 (0.12)
19	725	650	850	50	100	250	10.66 (0.58)
20	725	650	850	100	100	250	10.56 (0.31)
21	725	1100	850	50	100	250	7.56 (0.30)
22	725	1100	850	100	100	250	9.41 (2.17)
23	725	650	450	50	100	350	8.18 (0.58)
24	725	1100	450	50	100	350	7.88 (0.30)
25	725	650	450	100	100	350	9.20 (0.33)
26	725	1100	450	100	100	350	7.66 (1.25)
27	725	650	850	50	100	350	7.86 (0.66)
28	725	650	850	100	100	350	7.88 (0.68)
29	725	1100	850	50	100	350	6.23 (0.07)
30	725	1100	850	100	100	350	6.28 (0.06)

[a] The temperatures of the barrel and screw are in °F because they are set in this scale on the moulding machine. The temperatures were in the suggested range for PES: T_{barrel} = 700 to 750°F, 371 to 399°C; and T_{mould} = 250 to 350°F, 121 to 177°C

[b] Nominal speed of the screw

Fibre lengths and distributions were determined on a semi-automatic video interactive display system (VIDS) made by Optomax, Burlington, MA. This system was equipped with an Olympus BH2 microscope fitted with an Ikegami video camera, a Mitsubishi electric colour monitor, a digitizer pad equipped with a four-button cursor, an IBM PC XT model 286 computer loaded with the VIDS III software package for analysis of the data, and an IBM Proprinter XL. To obtain fibres for analysis of both their content and their lengths and distributions, previously moulded samples were dissolved in hot concentrated (36 N) sulphuric acid (Fisher Scientific), filtered and either weighed, for measurement of their content, or carefully transferred with a spatula to a glass slide (to avoid breakage of the fibres) for measurement of their lengths and distributions (a minimum of 250 fibres were measured).

Preparation and examination of the cross-sections of the samples involved mounting the samples in epoxy, sanding and polishing the surfaces using Buehler Autopolisher, and examining in a Nikon Epiphot type 104 microscope.

Statistical analysis of the measured resistivities was performed using step-wise multiple regression analysis. The resulting evaluation includes: the significant independent variables; their coefficients determined by the multiple regression analysis; their standard error; and the *r*-squared value.

RESULTS AND DISCUSSION

Table 1 presents the log(*SR*) values and their standard deviations for the samples with their conditions of moulding. For studies 1–16, pressures were either all high or all low, and we varied the temperatures of the barrel and mould and the power to the screw (screw speed). In conditions 17–30, the temperatures of the barrel and mould and the speed of the screw were constant, while the pressures (injection, holding and back) varied independently of each other. The values of log(*SR*) varied between 6.23 and 10.66.

Analysis of these data for statistically significant dependence of the conditions of moulding on log(*SR*) yielded the results in *Table 2*, both weighted and not weighted to the inverse of the standard deviations of the data. All important variables had a high degree of significance.

The results of this analysis showed that the injection pressure and the temperatures of the barrel and of the mould significantly influence the surface resistivity of the sample. The coefficients for the equation fitting the data for log(*SR*) of the moulded samples, weighted to the inverse of the standard deviations of the data, were: −1.90 for P_I (the coefficient is negative because *SR* decreased with increasing pressure); −1.25 for T_{barrel}; and −0.67 for T_{mould}. These variables were also significant when the data were not weighted to the standard deviation in the statistical analysis, and *Table 2* presents these coefficients as well.

Physical evaluation of moulded parts

In order to explain the physical significance of the effects of P_I, T_{barrel} and T_{mould} on *SR*, analysis of the samples made at the extremes of these conditions of moulding was necessary. This involved measuring the content of carbon fibres, the volume resistivity, and the length and distribution of the fibres both throughout the samples and at the surfaces. Although it is unlikely that the excellent correlation found from the statistical analysis is due to variation in the content of carbon fibres within the sample, measuring their content in those samples at the extremes in *SR* ensured that these measured differences in *SR* were not due to this potential variation. Measurement of the volume resistivities in these samples served as a further check on the content

Table 2 The dependence of significant variables on log(*SR*)

(a) Weighted to the inverse of the standard deviation in the data

Independent variable	Coefficient	Standard error
Constant	9.68	0.15
Temperature of barrel	−1.25	0.11
Temperature of mould	−0.67	0.10
Injection pressure	−1.90	0.14
r^2	−0.76	

(b) Not weighted to the inverse of the standard deviation in the data

Independent variable	Coefficient	Standard error
Constant	9.57	0.16
Temperature of barrel	−1.22	0.12
Temperature of mould	−0.60	0.11
Injection pressure	−1.69	0.17
r^2	−0.66	

of carbon fibres. We also measured the lengths of carbon fibres both throughout the samples and at their surfaces to see if a change in the length of fibre was responsible for differences in the *SR* values—a change in the length of carbon fibre would shift the percolation curve and thus shift *SR* for a fixed concentration of fibres. Finally, examination of the samples moulded at the extreme values of T_{mould} and P_I in cross-section was carried out to determine if a significant difference in morphology/distribution of fibre existed.

Content of carbon fibres

To ensure that the differences in *SR* were not due to variation in composition of fibre within the batch, we measured fibre content for those samples with the extreme values of log(*SR*). Samples 20 and 30 contain (5.3 ± 0.7) and $(6.2 = 0.2)$% carbon fibre, respectively; the contents of fibre were not significantly different for these two samples. Furthermore, the logarithm of the volume resistivities for samples 20 and 30 were also the same at 7.80 ± 0.39 and 7.73 ± 1.26 ohm cm, respectively. We do not, therefore, attribute the large difference in log(*SR*) of the moulded samples, and the excellent correlation in the statistical analysis of the data, to differences in the total content of carbon fibre.

Length of carbon fibres

If the differences in the surface resistivities of the samples are due to shifting of the percolation curve—requiring a higher content of shorter fibres for a sample with equivalent *SR*—due to breakage of the fibre under high shear conditions, the lengths and distributions of the carbon fibres in the moulded samples should show differences. Measurement of the fibre lengths throughout moulded discs in selected samples tested this hypothesis.

Previously, Karger-Kocsis and Friedrich[13] showed that, for samples of polyamide and glass fibres, the length of fibres was shorter at the surface compared to the core because of shear stresses experienced at the surface in moulding. If the length of the fibres at the surface contributes significantly to the surface resistivity, these differences should be observable in the lengths and distributions of the fibres at the surfaces of samples with significantly different log(*SR*) values. Examining the lengths of fibres and their distributions from surfaces of the selected discs allowed us to compare them with those throughout the sample. The measurement of length of fibres from the surfaces of the discs is qualitative because the same amount of material was not dissolved from the surface for each sample. A trend in these values, however, should indicate quantitative differences.

Table 3 presents the average lengths and distributions of fibres both from throughout the samples and from the surfaces of selected moulded discs. Because the distribution of fibre length is not Gaussian, we have presented the median and the mean to represent the degree of skewness of the data.

The physical characteristics of selected samples made under the extremes in conditions of moulding

The effect of injection pressure. Conditions of moulding for trials 28 and 30 differed in their injection pressures. Samples moulded under condition 30, using a high injection pressure, filled the mould faster at lower viscosity due to both shear thinning[14,15]—a lower viscosity from higher injection pressures—and less cooling—resulting in a lower viscosity than a colder sample—than did the samples moulded under condition 28. The later condition, 28, should therefore have experienced more shear in the mould, resulting in a greater degree of fibre breakage. The average length of fibres throughout the moulded sample is slightly shorter for the sample moulded under condition 28 than for condition 30, and this result is consistent with sample 30 being more conductive. Likewise, the average length of fibres from the surface is slightly shorter for the sample moulded under condition 28, 104 ± 63 μm with a mean value of 80–90 μm, than for that moulded under condition 30, 114 ± 77 μm and 90–100 μm. It is uncertain whether the average or the mean of the length of fibres governs the conductivity; however, evidence suggests that the presence of a smaller amount of longer fibres significantly influences the character of the percolation curve, resulting in a more conductive composite[16]. This result is also consistent with moulding condition 30, which produced samples with a lower log(*SR*).

Table 3 Fibre lengths and distributions from selected moulded samples

Sample	Fibre lengths (μm) Average	Standard deviation	Median	log(*SR*) (*SD*)
2	89	58	60–70	8.61 (0.54)
12	102	66	80–90	6.93 (0.20)
20	126	85	100–110	10.89 (0.12)
28	114	77	90–100	8.21 (0.86)
30	126	79	100–110	6.60 (0.03)
20, surface[a]	109	82	80–90	10.89 (0.12)
28, surface[a]	104	63	80–90	8.21 (0.86)
30, surface[a]	114	77	90–100	6.60 (0.03)

[a] To analyse fibres from the surface, we dissolved the surface of the sample with methylene chloride, collected enough fibres to analyse, and removed the moulded disc to avoid dissolving and collecting fibres from the core of the sample

The effect of temperature of the barrel. The conditions of moulding for settings 2 and 12 differed in the temperature of the barrel: condition 12 was at a higher temperature than was 2. The lower temperature for condition 2 most likely caused higher shear in the barrel, resulting in more fibre breakage compared with the sample run at the higher temperature, condition 12. The standard deviations of the fibre lengths are large; nevertheless, the average and median fibre lengths of the sample moulded under condition 12 are slightly larger than those for condition 2. A higher percentage of longer fibres, as in the sample made under condition 12, may have a significant influence on the electrical properties of the composite. The higher log(*SR*) for condition 2 is consistent with the shorter fibres found in this sample.

The effect of temperature of the mould. The T_{mould} for moulding condition 28 was higher than for 20. The material moulded at the higher temperature should have experienced less shear during moulding than that which was run at a lower temperature. Although the average fibre lengths for fibres throughout the parts are longer for the less conductive sample, condition 20, at 126 ± 85 μm, compared with 114 ± 77 μm for condition 28, there are no significant differences in the fibres at the surfaces of

the samples moulded under conditions 28 and 20, 104 ± 63 and $109 \pm 82\,\mu m$ respectively, and their median lengths are the same at 80–90 μm. Therefore, differences in the values of log(SR) must be due to factors other than length of fibre. Possibly a difference in content of fibre at the surface could account for the difference in SR for these samples.

The effect of both the injection pressure and temperature of the mould. The fibre lengths and distributions of fibres in the samples with settings at the extreme values of both P_I and T_{mould}, conditions 20 and 30, were not significantly different from each other at 126 μm, median lengths 100–110 μm. However, the lengths of the fibres at the surface of the samples, shorter than those in the centre, are slightly longer for the more conductive sample, 30: for samples moulded under condition 20, the average length of fibre is $109 \pm 82\,\mu m$ and the median is 80–90 μm; for samples moulded under condition 30, the values are $114 \pm 77\,\mu m$ and 90–100 μm. Both the lower injection pressure and the lower temperature of the mould for samples moulded under condition 20 could contribute to its higher log(SR). Because the percolation curve for longer fibres shifts to higher conductivity for a given concentration of fibres, the presence of longer fibres at the surface in samples moulded under condition 30 is consistent with a more conductive sample.

Morphology of the moulded discs

Differences in content of fibre at the surface and their orientation may also contribute to the observed differences in SR. To test this hypothesis, we prepared cross-sections of samples moulded under conditions 20 and 30, from the centre of the disc and perpendicular to the direction of flow in the mould. We chose this orientation because the sample is aligned so that the electrodes for measurement of log(SR) are parallel to the direction of flow and 1/4 inch (6 mm) from the centre of the disc on either side. The fibres for both samples were oriented in the direction of flow. In the centre of the samples, some variation of fibre orientation occurred; however, a well defined core did not exist for either sample. We saw no significant difference in orientation of fibres at the surfaces of either sample. Possibly, some differences in orientation exist further from the centre of the disc, and this may account for some of the differences in log(SR) that we observed.

Figure 1 shows the results of examination of the cross-sections of samples moulded under conditions 20 and 30 with a plot of the content of fibres for both samples as a function of depth from the surface. The content of fibres for samples moulded under condition 20 are slightly lower through a depth of approximately 500 μm than for those moulded under condition 30. The lower concentration of carbon fibres at the surface for condition 20 is consistent with the higher log(SR) that we observed from these samples.

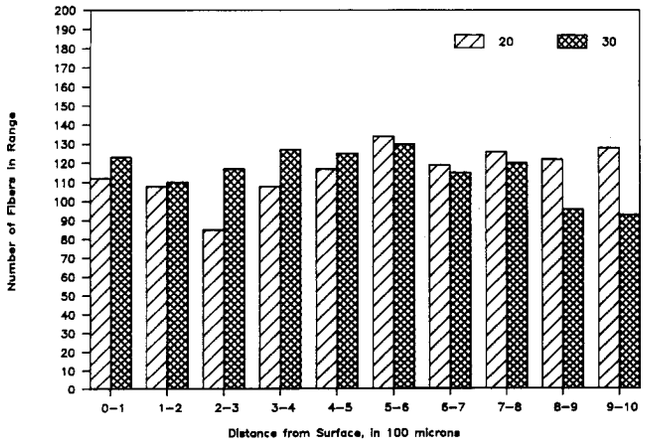

Figure 1 A plot of the relative content of carbon fibres *versus* distance from the surface of the sample for samples moulded under extreme conditions of both P_I and T_{mould}: 20, minimum settings, and 30, maximum settings

CONCLUSIONS

We make the following observations.

The condition of moulding significantly affected the resulting log(SR), ranging between 6.23 and 10.66, for a single batch of a PES/carbon-fibre composite.

The significant variables in moulding are temperature of the barrel, T_{barrel}, temperature of the mould, T_{mould}, and injection pressure, P_I.

As they increase, these variables decrease log(SR) at the extreme values of their settings, with coefficients of -1.90 for P_I, of -1.25 for T_{barrel} and of -0.67 for T_{mould}.

Samples made under conditions at the extreme settings of T_{barrel} exhibit differences in their average and median fibre lengths; those made under conditions of lower T_{barrel} have shorter fibres. Presumably a higher shear stress, caused by an increase in the viscosity of the material that was run at lower temperatures, contributed to an increase in the breakage of fibres. The samples moulded at lower T_{barrel} have higher log(SR) values, and this result is consistent with the presence of shorter fibres in the sample.

Fibres from the surfaces of samples moulded at different T_{mould} values had fibre lengths and distributions that were not significantly different in length. The differences in log(SR) for samples moulded at the extreme values for T_{mould} must be due to factors other than the length of carbon fibres, such as content of carbon fibre.

Samples moulded with a higher injection pressure had slightly longer fibres. Apparently, with a higher pressure, the sample flowed faster, filled the mould quicker, and had less time to cool and increase in viscosity prior to filling the mould. The resulting shear stress must be less than for a sample moulded with a lower injection pressure. The shorter fibres found in samples that have been moulded at lower injection pressures are consistent with their higher log(SR).

Examination of cross-sections of moulded samples made under conditions 20 and 30 revealed that the distribution of carbon fibres near the surface was lower for sample 20. This result is consistent with the higher surface resistivity in this sample. Although the orientation of the fibres can influence the surface resistivity of the sample, the samples examined here showed no significant difference in the orientation of the fibres.

Finally, it appears that conditions of moulding influence not only the lengths and distribution of carbon fibres but also the distribution/relative concentration of fibres at the surface. These resulting morphological effects influence the resistivity at the surface of the moulded sample.

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