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Computer simulation of electrical conductivity of graphite-based polypropylene composites based on digital image analysis

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Abstract The electrical conductivity of polypropylene/graphite (PP/G) composites and polypropylene/graphite/carbon black (PP/G/CB) composites was investigated in this article. A simulation procedure, which is not limited to any specific parameters (i.e. graphite size and shape), was used to numerically compute the electrical conductivity of the composites. The simulations were carried out using a 2D finite element program based on the digital image analysis. The simulation results were in good agreement with the experimental conductivity values even though there were several limitations in using digital image analysis such as sampling, sample preparation, the quality of the image and the choice of the threshold. The microstructures of the surfaces of the composites were observed using scanning electron microscopy (SEM).

Introduction

The problem of the electrical conduction in conductive polymer composites (CPCs) is an old and difficult one because the electrical conductivity in such heterogeneous systems can lie anywhere between the conductivities of the components depending both on the volume fractions of the components, and the morphology of the medium [1]. The electrical conductivity is dependent on a number of factors, including filler particle shape, size and distribution, and the ability to form homogeneous mixtures on combination with resin [2, 3]. Various models have been proposed in an effort to predict the electrical conductivity behaviour of composites based on numerous factors. There are four main classes of conductivity models found in literature, and they include statistical, thermodynamic, geometrical and structure-oriented models, as described in detail by Lux [4].

These models successfully represented the electrical behaviour of CPCs as reported in the literature [5–9]. However, it was shown by Clingerman [10] that there were limitations within each model that can significantly affect the calculations. Therefore, it is more useful to have a simulation procedure which is not limited to any specific parameters. A numerical approach offers such a solution. To numerically compute the electrical conductivity of such materials requires knowledge of the microstructure. The microstructural information is almost always in 2D or 3D digital images form, collections of discrete square or cubic pixels in which each pixel can, in principle be different phase of the material. Hence, there is a need to have computer programs that are specialised to work on digital images. Such work has been cited in the literature to compute the effective properties of composite materials [11–15].

In order to analyse images on the computer, one utilizes digitised representations of the samples, i.e. two- or three-dimensional arrays of grey values spanning the finite system, typically subjected to periodic boundary conditions. For a two-phase material, the grey-scale image can be reduced to a binary image by operations such as thresholding, in which grey values lighter than a chosen threshold are set to white and the others set to black. The image is thus reduced to an array of bits or pixels (voxels). On other words, a single image (described as a frame) is divided into a grid small square cells, or pixels (picture

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elements) a typical frame may contain 512 pixels × 512 pixels. Each pixel is examined separately by the image analyser and may be described by its *x*- and *y*-coordinates plus a digitised 'grey level' which describes its shade between black and white. The grey level assigned to an individual pixel (typically the scale is divided into 256 grey levels) may be altered to enhance the image. The enhanced grey image is then available for image analysis. If distinction between two phases is needed such as between fibres and matrix in fibre-reinforced composite, 'threshold' grey level is chosen.

The aim of this work was to provide an overview of the use of computer-based techniques for image analysis in a microscopical study of polypropylene/graphite (PP/G) composites. Then, after analysing the digital images of the microstructures, it can be read into a 2D finite element program to predict the electrical conductivity of these composites. The maximum electrical conductivity of polypropylene/graphite/carbon black (PP/G/CB) composites can also be predicted from the PP/G image analysis. The simulation results were also compared with the experimental conductivity data of the composites.

Experimental

Materials

Synthetic graphite powder used in this study had a density of 1.8 g/cm^3, an electrical conductivity of 772.2 S/cm, and an average particle size of 10 μm. It was supplied by GME Carbon Sdn. Bhd., Malaysia. Carbon black N330 (HAF) was purchased from Cabot Sdn. Bhd., Malaysia, with the following specifications: 30 nm particle size, 1.7–1.9 g/cm^3 density, 2.93 S/cm electrical conductivity and 254 m^2/g surface area. Polypropylene (PP) grade Titan (600), 910 kg/m^3 and 10 g/10 min, was supplied by Polypropylene Malaysia Sdn. Bhd.

Preparation of PP/G and PP/G/CB composites

The components of the composites were melt compounded in a Haake batch mixer at a temperature of 175 °C. The rotational speed and the mixing time were set at 35 rpm and 10 min, respectively. The composites obtained after mixing were pulverised to powders in order to improve homogeneity of the samples. These powders were put in a mould, preheated in a hot press machine for 10 min, and then hot pressed into discs of 25 mm diameter and 2 mm thickness at a temperature of 200 °C and a pressure of 75 kg/cm^2 for 3 min for the purpose of electrical conductivity measurements. The composition of G was fixed to 80 wt.% in all composites.

Characterisations

DC conductivity measurements

The conductivities of the discs in the plane direction were measured by means of a Jandel Multi Height Four-Point Probe combined with RM3 Test Unit which had constant current source and digital voltmeter designed especially for the four point probe measurement. This technique measured sheet resistance in the range from 1 milliohm-per-square up to 5×10^8 ohms-per-square and volume conductivity range from 10^{-6} to 10^3 S/cm. The system accuracy was within 0.3%.

Morphological observations

The polished surface morphologies of the composites were investigated by using variable-pressure scanning electron microscope (VPSEM, Model LEO 1450VP) at an accelerating voltage of 20 kV. The samples were gold-sputtered prior to the SEM examination. Backscattered electrons were utilised to provide atomic number contrast between the composite components.

Results and discussion

Conductivity measurements

The experimental electrical conductivities of the composites are shown in Fig. 1 and summarised in Table 1. The reported values represented the average of five readings. The conductivity of the composites was observed to increase from 7 S/cm at 0 wt.%CB to 72 S/cm at 15 wt.%CB. The SEM surface micrographs of PP/G composites in Figs. 2–4 showed that G particles aggregated

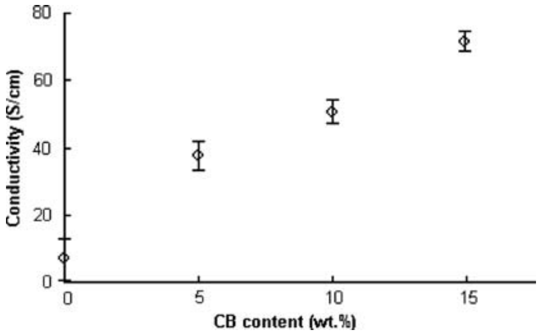

Fig. 1 Conductivity vs. CB content in PP/G/CB composites at 80 wt.%G

Table 1 Experimental values of conductivities of PP/G and PP/G/CB composites

wt.%G	wt.%CB	wt.%PP	σ (S/cm)
80	0	20	7.01
80	5	15	37.79
80	10	10	50.43
80	15	5	71.40

wt.% is the weight percent and σ is the electrical conductivity

into larger low-aspect-ratio clusters. These tended to disperse more evenly into the PP, thereby resulting in fewer particle–particle contacts and, consequently, a lower-conductivity polymer composite. Combination of G with a minor weight fraction of CB introduced a synergy effect, resulting in a significantly higher conductivity than with single G filler. The conductive network built up by the binary filler system is assumed to consist of highly dispersed CB particles bridged by G particles [16, 17].

Microstructural image analysis and computer simulation of conductivity

To analyse the digital images of the microstructures, electron scanning micrographs have been taken at different magnifications; 100×, 200× and 500×, for the surface of PP/G composite containing 80 wt.%G. Six micrographs or samples have been taken at each magnification. They then analysed using image processing software (MatLab). In the image processing, the choice of threshold to produce a binary image with the polymer in white, and the filler being black was critical. To successfully run the program, the conductive phase (i.e. graphite) has to be connected (percolated); otherwise negative values were obtained for the conductivity and this considered as a disadvantage of this program since it did not take into consideration the tunnelling effect. Thus, the threshold value was chosen as the minimum value, which needed to create a connected path of G in each image and this was considered as the percolation criterion. The results after analysing the digital

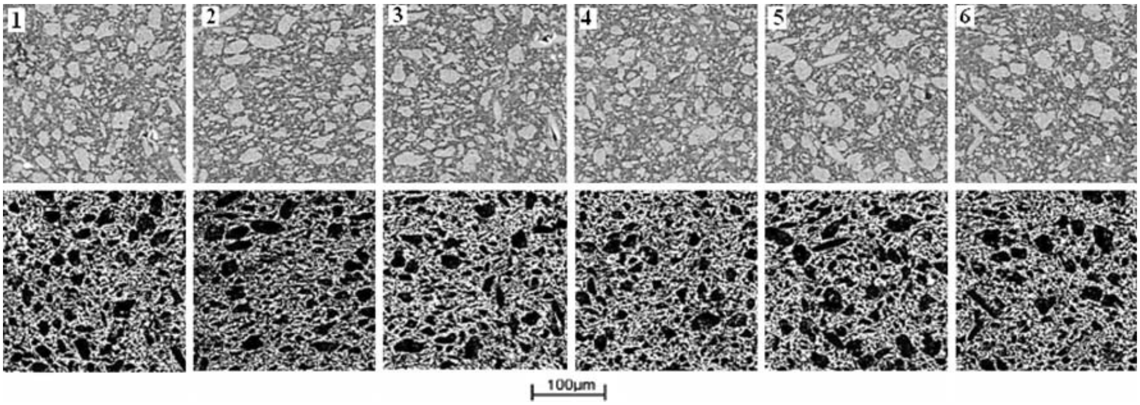

Fig. 2 Grey images of PP/80 wt.%G surface micrographs and their binary images (black and white) at a magnification of 100×

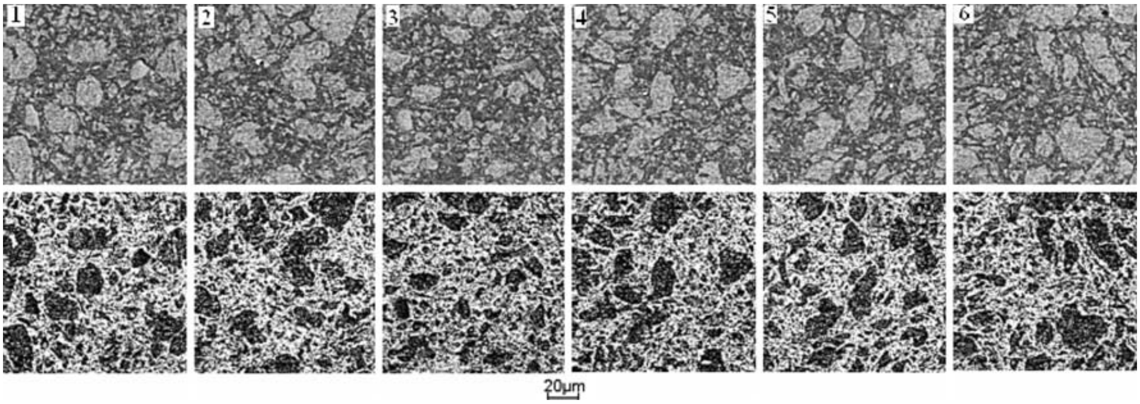

Fig. 3 Grey images of PP/80 wt.%G surface micrographs and their binary images (black and white) at a magnification of 200×

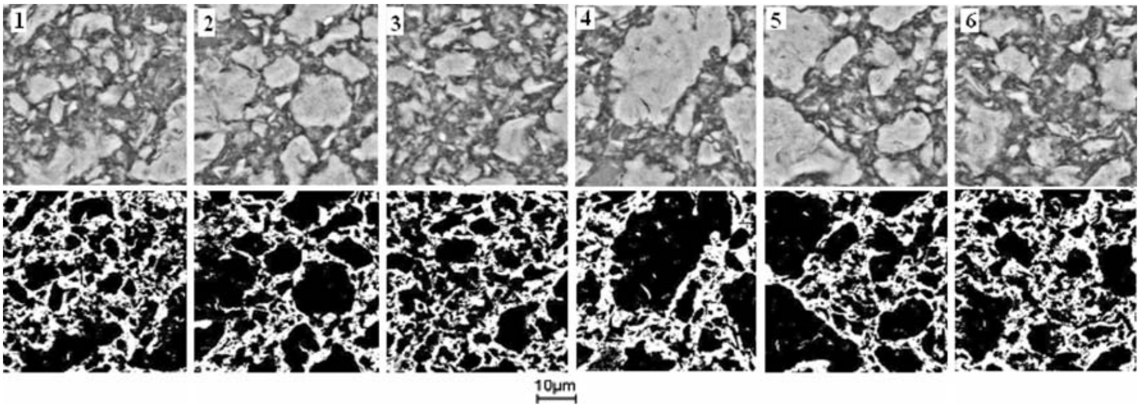

Fig. 4 Grey images of PP/80 wt.%G surface micrographs and their binary images (black and white) at a magnification of 500×

images of the microstructures are shown in Figs. 2–4. These figures represented the grey images and their binary images (black and white). The size of the images was 256 × 256.

Then, after analysing the digital images of the microstructures it can be read into a 2D finite element program to compute the conductivity of the composites. This program which is written in FORTRAN has been proposed by Garboczi [18] to calculate the effective conductivity of a material composed of different conducting and non-conducting phases. The conductivity of each phase was set before running the program to σ_1 = 772.2 S/cm for phase 1 (i.e. G) and $\sigma_2 = 10^{-14}$ S/cm for phase 2 (i.e. PP). The area fractions of G phase and the conductivity in *x*- and *y*-directions for the eighteenth samples are summarised in Table 2.

It was noticed from Table 2 that reasonable values for conductivity could be obtained from the simulations compared to the actual conductivity measured for PP/80 wt.%G composite (7 S/cm). No trend in the three magnifications could be noticed except that the values of area fraction and conductivity were slightly higher at 500× than at 100× or 200×. This was attributed to the maximisation of the image which resulted in increasing the G fraction area and hence the conductivity. So that, it was concluded that a lower magnification is preferable for more accurate conductivity measurements.

Table 2 Simulation results of conductivities of PP/80%G and area fractions of G, which obtained by assuming that the white area in the binary images in Figs. 2–4 is PP phase and the black area is G phase

Magnification	Sample number	Area fraction of G	σ_x (S/cm)	σ_y (S/cm)
100×	1	0.576	13.79	19.86
	2	0.594	3.23	14.39
	3	0.565	7.23	20.09
	4	0.580	8.89	6.10
	5	0.591	6.64	19.92
	6	0.590	9.12	49.78
Mean value ± SD		0.582 ± 0.011	8.15 ± 3.48	21.69 ± 14.79
200×	1	0.539	12.11	12.54
	2	0.540	11.30	18.47
	3	0.559	10.99	34.99
	4	0.577	26.79	11.18
	5	0.521	11.81	9.41
	6	0.563	9.44	18.28
Mean value ± SD		0.566 ± 0.020	13.74 ± 6.46	17.47 ± 9.35
500×	1	0.649	33.00	18.50
	2	0.704	10.05	50.79
	3	0.639	24.46	9.54
	4	0.678	24.76	21.97
	5	0.728	28.03	2.98
	6	0.638	16.09	29.16
Mean value ± SD		0.672 ± 0.037	22.73 ± 8.13	22.15 ± 16.78

SD is the standard deviation and σ_x, σ_y are the conductivity in *x*- and *y*-directions of the images

Predicting the conductivity of PP/G/CB composites using computer simulation

If CB was added to the PP/80 wt.%G composite that studied in the previous section; to what extent the electrical conductivity could be increased?

Actually, the thought was that CB behaved as "bridge" to connect the G particles in the PP/G composites as mentioned earlier. Thus, to predict the maximum conductivity when incorporating CB to PP/80 wt.%G composite, the CB was assumed to fill the white area in the binary images of the PP/80 wt.%G, which are shown in Figs. 2–4. The conductivity of each phase was set before running the program to σ_1 = 772.2 S/cm for phase 1 (i.e. G) and σ_2 = 2.93 S/cm for phase 2 (i.e. CB). There assumed no PP

Table 3 Simulation results of conductivities and area fractions of G, which obtained by assuming that the white area in the binary images in Figs. 2–4 is CB phase and the black area is G phase

Magnification	Sample number	Area fraction of G	σ_x (S/cm)	σ_y (S/cm)
100×	1	0.576	54.90	80.56
	2	0.594	44.99	93.97
	3	0.565	46.75	74.98
	4	0.580	47.66	91.91
	5	0.591	47.67	95.22
	6	0.590	56.05	106.42
Mean value ± SD		0.582 ± 0.011	49.67 ± 4.61	90.51 ± 11.21
200×	1	0.539	53.34	64.74
	2	0.540	18.39	95.72
	3	0.559	69.17	110.57
	4	0.577	70.69	86.15
	5	0.521	45.60	51.99
	6	0.563	58.34	80.35
Mean value ± SD		0.566 ± 0.020	52.59 ± 19.25	81.59 ± 21.08
500×	1	0.649	66.24	68.37
	2	0.704	73.69	113.95
	3	0.639	48.81	105.97
	4	0.678	66.35	70.82
	5	0.728	98.10	143.95
	6	0.638	64.82	81.50
Mean value ± SD		0.672 ± 0.037	69.66 ± 16.16	97.42 ± 29.38

SD is the standard deviation and σ_x, σ_y are the conductivity in *x*- and *y*-directions of the images

phase existing in the binary images and this assumption was reasonable since the maximum value was of interest. The area fractions of each phase and the conductivity in *x*- and *y*-directions were computed from the simulations and the results are shown in Table 3.

The maximum experimental conductivity of PP/G/CB composites, which obtained at 80 wt.%G and 10 or 15 wt.%CB was in good agreement with the predicted values. The difference between the two values resulted from neglecting the PP phase in the composites.

Finally, the inaccuracies in measurements raised from sampling, sample preparation, the quality of the image and the choice of the threshold. Ideally, maximum contrast between the two phases must be introduced in the preparation of the sample and the back-scattered SEM might not give good enough contrast, as the contrast come from differences in atomic number. Graphite and PP have similar atomic numbers (carbon). The quality of the image, including the focal depth of the microscope may often introduce a gradual change in the grey level between the two phases. Measured fraction area and hence the conductivity were affected by the precise threshold chosen. The exact choice of threshold thus determined the size of detected features, and thus the real measurements.

Conclusion

The computer simulation showed reasonable conductivity results even there were several limitations in using digital image analysis such as sampling, sample preparation, the quality of the image and the choice of the threshold. However, if careful consideration is given in the future to these possible limitations, then the affect could be significantly decreased and the results will be more accurate than if features were measured without the aid of digital processing techniques.

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