Effect of Foaming on Fiber Orientation and Electrical Conductivity of Polymer Carbon Fiber Composites in Injection Molding

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Introduction

Numerous applications of electrically conductive polymer composites have initiated a very active research area to develop these materials. Addition of conductive fillers such as carbon fiber and carbon black to a non-conductive thermoplastic matrix by melt mixing is one of the common approaches to produce conductive polymer composites. Injection molding is the favoured method to produce electrically conductive parts. Flow induced fiber orientation during mold filling and packing results in anisotropic properties for molded composites [1]. Previous studies show that anisotropic fiber orientation exhibit anisotropic conductivity changes by up to 3 orders of magnitude, parallel and perpendicular to the flow direction [2-3]. Therefore tailoring of fiber orientation distribution to obtain the desired electrical conductivity in the preferred direction is a requirement in the processing of electrically conductive polymer/carbon fiber composites. In this research we have investigated the impact of foaming along with processing conditions on fiber orientation and electrical conductivity of cyclic olefin copolymer (COC)/carbon fiber (CF)-carbon black (CB) hybrid composites in injection molding process. A fractional factorial design was used to screen the effects of injection speed, melt temperature and mold temperature with and without foaming. Cell size distribution, fiber orientation distribution, fiber length and electrical conductivity in three dimensions were characterized. The results revealed that foaming can enhance the conductivity in the transverse and normal direction to the mold flow. Foaming reduces injection shot size and viscosity resulting in lower injection pressure; therefore foaming can expand the application of injection molding for composites with high filler loading.

Experimental

Materials

Cyclic olefin copolymer (COC), Topas 6013S-04 (supplied by Ticona), with MFR(260°C, 2.16 kg)=14 cc/10min and T_g=140 °C was used as polymer matrix. Unsized chopped carbon fiber, AGM-94 (Asbury Carbons), with nominal length of 6 mm, diameter of 7.5 microns and electrical conductivity of 625 S/cm, and carbon black, KetjenBlack EC600JD (AkzoNobel) with nominal aggregate size of 30-100 nm, BET surface area of 1250 m^2/g and electrical conductivity of 10-100 S/cm were used as conductive fillers. A masterbatch of 5-Phenyl tetrazol (PHT), IM 2240 (Dempsey Corporation), with 20% active PHT and nominal activation temperature of 240 °C was used as chemical blowing agent (CBA).

Compounding and Molding

45%v/v concentrate of chopped carbon fiber (CF) in COC was prepared in a Haake batch mixer and pelletized in a grinder to be used as CF precursor for the next phase. A modular corotating twin screw extruder (TSE), Lestritz ZSE 27 mm L/D=40 (10 blocks), was used to produce the composite. The screw speed was set at 100 rpm and the temperature profile was 260 °C for blocks 2-9 and 250°C for block 1 and die. COC and carbon black (CB) were fed to the first block of the TSE by a weight-loss feeder, and CF precursor was

fed by a side stuffer to the 5th block. The screw configuration was set at very low shear for block no. 5 and after to minimize the fiber breakage. The feeding rates and proportion of COC and CB in the first feeder was adjusted proportionally so that a COC compound with 10%$_{v/v}$ CF and 2.5%$_{v/v}$ CB can be achieved. At the end of production all the collected pellets were thoroughly mixed to obtain a homogenous material for injection molding.

Arburg 55 ton injection molding machine with screw diameter of 30 mm, L/D=20 and five temperature controllable zones, was utilized to make rectangular plaques 14.5cm × 3 cm × 0.3cm. A half fractional factorial design as shown in Table 1 was used to produce foamed and non-foamed samples at different processing conditions including injection speed, extruder temperature and mold temperature, at two levels. Other processing factors were kept constant for all runs except packing pressure which was set at 500 bar for all non-foamed runs and 0 bar for all foamed runs. To produce foamed samples IM2240 pellets were dry blended with the composite pellets and fed to the hopper. The onset of decomposition for CBA used in this study was determined by TGA analysis to be 225 ℃. Therefore the temperatures of the first three zones on the extruder, was always set below 220 ℃ to prevent premature decomposition of CBA and gas loss while the temperatures of the last 2 zones on the extruder and nozzle temperature was always set above 240 ℃ to obtain full decomposition. The injection nozzle was also equipped with a shut-off nozzle to prevent gas and melt loss during injection.

Table 1. Half Fractional Factorial Design

Run	IM2240 (%$_{w/w}$)	Injection Speed (cc/s)	Melt Temperature (℃)	Mold Temperature (℃)
1	0	10	260	80
2	0	10	300	120
3	0	100	260	120
4	0	100	300	80
5	5	10	260	120
6	5	10	300	80
7	5	100	260	80
8	5	100	300	120

Sample Preparation and Analysis

The injection molded plaques were cut to 3.75 mm × 27 mm rectangles and 20mm disks according to patterns shown in figure 1. Electrical conductivity was measured in the length (L), width (W) and thickness (T) directions of the plaques. Four-probe method (see Fig. 2b) was used to measure the electrical conductivity in the L and W directions while two-probe method (see Fig. 2a) was used to measure it in the T direction. In all measurements a constant current was applied to the gold coated copper electrodes and voltage was measured at a distance of 15 mm between voltage probes for L and W measurements and on the copper electrodes for T measurements. In 2-probe method to impart good contact, carbon paper was placed between electrodes and the sample and 3.1 KN constant compressive force applied to the resultant sandwich.

T2B samples were mounted in epoxy resin and polished by Struers automatic polisher at the skin and core level. The polished samples were analyzed under reflected light microscopy to measure fiber orientation at the skin and core level. Cell size distribution was also obtained from the core level. At least 500 fibers or cells were measured.

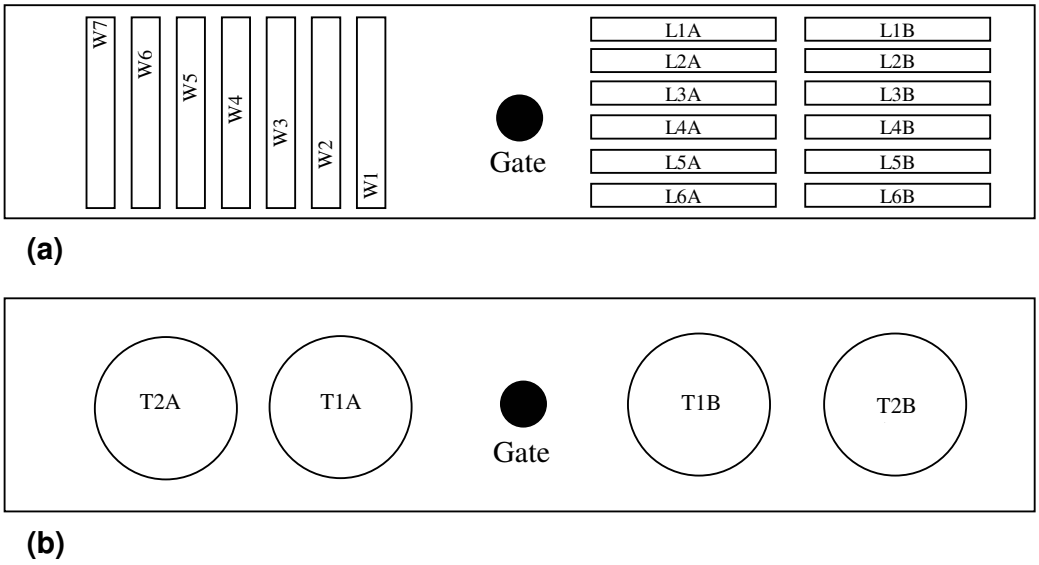

Fig. 1 Cutting pattern to prepare samples for electrical conductivity measurements: (a) samples for longitudinal and transverse measurements and (b) samples for through-plane measurements

To measure fiber length distribution, about 0,5 g of composite sample was pyrolized in an electrical furnace and the obtained ash was dispersed in xylene, coated on glass slides and left in the fume hood to dry. Then slides were analyzed by transmitted light microscope to take enough images. The lengths of three sets of minimum 500 fibers were measured by SigmaScan Pro 3.0 software for each sample. The density of the samples was also obtained by buoyancy procedure.

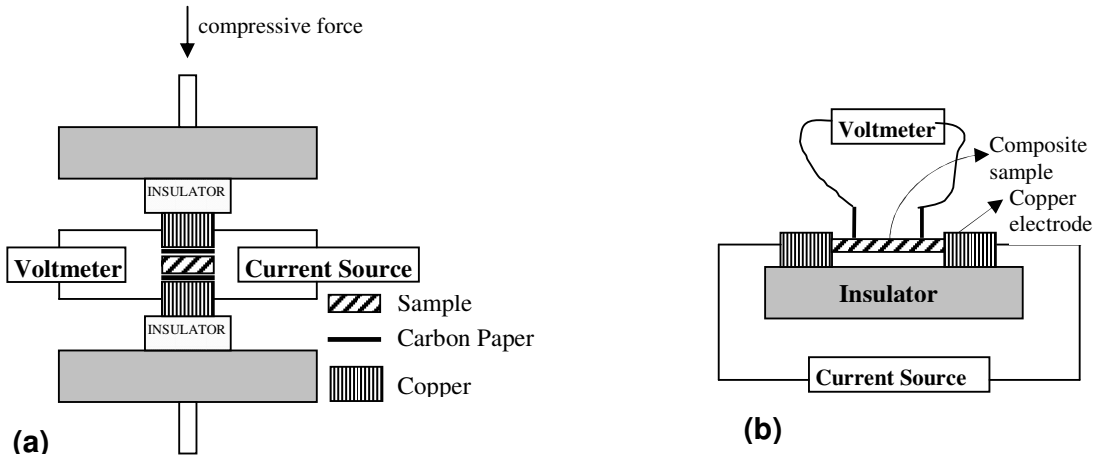

Fig. 2 Schematic diagram of the set-up for electrical conductivity measurement (a) 2-probe method and (b) 4-probe method

Results and Discussion

Table 2 and 3 represent the results for electrical conductivity and microstructural properties of the composites produced by inection molding according to the conditions in table 1. Considering table 2a or 2b ($\sigma_{average(LWT)}$), the highest conductivity value belongs to run (6) which is a foam composite. Furthermore average conductivity values for non-foam and foam runs shows higher conductivity for the latter. Yang and Gupta who studied the effect

of foaming on electrical conductivity of polystyrene carbon nanofiber composites by solution casting have reported similar conclusions [4]. They found that foam composites have similar conductivity to solid composites. This could be due to the effect of ingredients in IM2240 or residue of CBA in the foam samples. We prepared the same compound as used for injection molding, with and without IM2240, in a batch mixer. No significant difference was observed between conductivities of the sample with IM2240 and the one without it. Moreover by adding 5% IM2240 to the conductive compound, the volume fraction of the conductive filler is decreased (about 0.5% $_{v/v}$ in 12.5% $_{v/v}$) and this could lead to a decrease in conductivity not increase.

The last two columns in Table 2a or 2b represent anisotropy of the composites. As expected the highest conductivity is in the main direction of the flow (L) followed by transverse direction of the flow (W) and perpendicular to the main flow (T). This is in agreement with fiber orientation distribution in Table 3. θ is the angle of fibers with the flow direction in LW plane while ϕ is the angle that fibers make with T direction. In addition looking at σ_L/σ_W and σ_L/σ_T average values for foam and non-foam runs reveals that the L/W anisotropy is low and very similar for both but it is very intense for L/T case where foams

Table 2. Electrical conductivity results for factorial design injection molded samples in L, W and T directions: (a) close to the gate and (b) far from the gate (according to Fig. 1). *Note: all average values for conductivity are geometrical averages*

(a)	Run	$\sigma_{L3B-L4B}$	σ_{W5-W6}	$\sigma_{T2A-T2B}$	$\sigma_{average(LWT)}$	σ_L/σ_W	σ_L/σ_T
		(S/cm)					
non-foam	1	6.7E-05	3.0E-05	1.2E-06	1.3E-05	2.2	55
	2	4.3E-04	1.2E-04	1.2E-06	4.0E-05	3.5	350
	3	6.8E-03	1.0E-02	2.5E-05	1.2E-03	0.7	273
	4	3.3E-02	1.1E-02	9.5E-05	3.2E-03	3.0	343
foam	5	1.9E-02	9.0E-03	9.0E-06	1.2E-03	2.1	2108
	6	2.6E-02	2.2E-02	2.9E-04	5.5E-03	1.1	87
	7	4.3E-04	1.4E-04	2.6E-07	2.5E-05	3.0	1655
	8	2.4E-02	3.7E-03	3.4E-06	6.7E-04	6.4	6876
Average	*non-foam*	*1.6E-03*	*7.9E-04*	*7.7E-06*	*2.1E-04*	*2.4*	*255*
	foam	*8.4E-03*	*3.2E-03*	*7.0E-06*	*5.7E-04*	*3.1*	*2681*
	total	*3.6E-03*	*1.6E-03*	*7.3E-06*	*3.5E-04*	*2.3*	*498*

(b)	Run	$\sigma_{L3A-L4A}$	σ_{W1-W2}	$\sigma_{T1A-T1B}$	$\sigma_{average(LWT)}$	σ_L/σ_W	σ_L/σ_T
		(S/cm)					
non-foam	1	6.0E-05	1.5E-05	3.6E-07	6.8E-06	4.1	168
	2	8.4E-04	2.5E-04	1.9E-05	1.6E-04	3.4	45
	3	3.6E-03	5.6E-03	2.8E-05	8.3E-04	0.7	128
	4	2.7E-02	1.8E-02	7.2E-05	3.3E-03	1.5	381
foam	5	6.2E-03	4.4E-03	1.2E-06	3.2E-04	1.4	4993
	6	3.6E-02	3.0E-02	1.3E-04	5.2E-03	1.2	275
	7	4.5E-03	1.8E-03	1.0E-07	9.4E-05	2.4	44811
	8	2.5E-02	8.1E-03	2.0E-06	7.4E-04	3.1	12658
Average	*non-foam*	*1.5E-03*	*7.8E-04*	*1.1E-05*	*2.3E-04*	*2.4*	*181*
	foam	*1.3E-02*	*6.7E-03*	*2.4E-06*	*5.8E-04*	*2.0*	*15684*
	total	*4.3E-03*	*2.3E-03*	*5.1E-06*	*3.7E-04*	*1.9*	*856*

have even significantly higher anisotropy. Average conductivities in the L, W and T direction for foam and non-foam runs show higher conductivity for the foamed samples in the L and W direction but less in T direction. This could be due to the fact that the conductive network in the T direction is very close to the percolation point and introducing non-conductive gas voids can drastically disconnect conductive paths through the T direction. Comparing run 6 with other runs says that it has even the highest conductivity in the T direction while it is foam composite. According to Table 3, sample (6) has the finest average cell size than other foam samples (see Fig. 3).

Table 3. Fiber orientation, length and density of the composites at T2 location

	Run	θ	Φ	Length	Density	Cell Size (μm)		
		(°)	(°)	(μm)	(g/cc)	Average	Max.	Min.
non-foamed	1	40	76.7	101±3	1.10			
	2	36	75.0	98±11	1.11			
	3	40	77.7	102±7	1.11			
	4	47	75.1	102±3	1.10			
foamed	5	37	68.9	94±3	0.90	30	362	7
	6	51	72.2	98±1	0.92	20	123	7
	7	37	76.8	106±1	0.91	35	312	7
	8	32	74.8	105±6	0.91	23.3	238	7

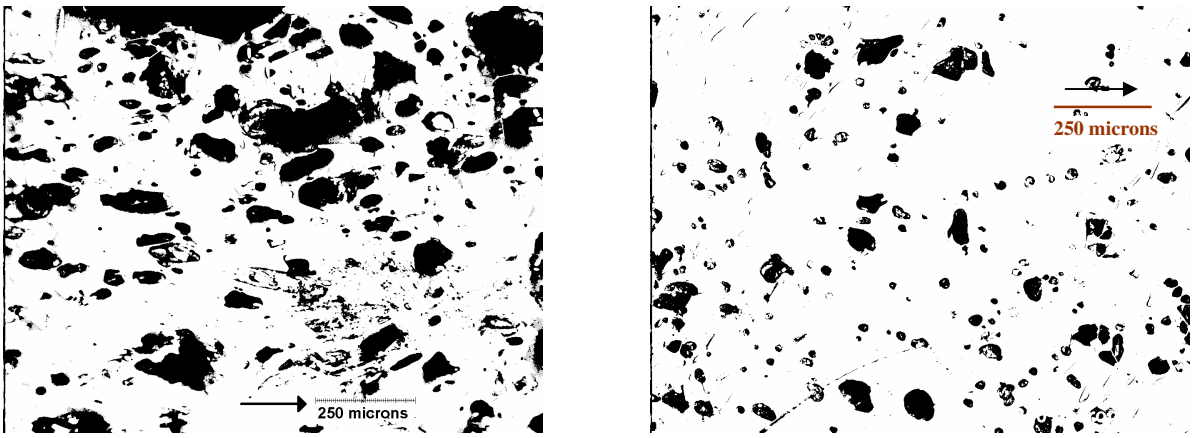

Fig. 3. Micrographs of the foam injection molded samples obtained from polished T2B samples by reflected light microscopy: left: run (5) and right: run (6)

Composites with CBA powder

According to the results obtained from the factorial design, a suitable processing condition was chosen for further investigation on foaming (Table 4). One non-foam and two foam composites with different level of foaming were produced. In this set of experiments, instead of PHT concentrate (IM2240), PHT powder with 99% purity was added to the composite pellets at 2%$_{wt}$ prior to injection molding as blowing agent. Use of pure PHT is useful in terms of adding high CBA without introducing a large decrease in the conductive filler content but also having much less inorganic residue, compared to using IM2240 concentrate. Samples were cut from the area between gate and end of the cavity similar to Figure 1 for analysis.

As seen in Table 5, foaming improves not only the average electrical conductivity but also through-plane conductivity. Higher degree of foaming, when comparing B and C composites, provides even more improvement of electrical conductivity in the W and T

direction. Conductivity in the T direction has improved more than 1 order of magnitude from sample A to sample C. Micrographs in Fig. 4 demonstrate that, for non-foamed sample, fibers are more oriented in the flow direction compared with foamed sample. In addition some oriented fibers in the T direction can be detected in the foam sample. Injection pressure for foamed samples is lower than non-foam sample. It is well studied that viscosity of polymer/gas mixture is lower than pure polymer melt which can lead to lower injection pressure [5].

Table 4. Injection molding conditions for second set of composites

Run	Injection speed (cc/s)	Melt temperature (℃)	Mold Temperature (℃)	CBA content ($\%_{w/w}$)	Shot size (%)	Injection Pressure (MPa)
A	4	280	80	0	100	370
B				2	86	285
C				2	78	280

Table 5. Electrical conductivity of the composites with CBA powder

Run	Density	σ_L	σ_W	σ_T	$\sigma_{Average}$	σ_L / σ_W	σ_L / σ_T
	(g/cc)	(S/cm)					
A	1.12	1.2E-02	2.7E-03	1.6E-05	8.2E-04	4.6	761
B	1.01	3.5E-02	2.3E-02	1.4E-04	4.9E-03	1.5	246
C	0.91	1.1E-02	2.6E-02	5.6E-04	5.4E-03	0.4	20

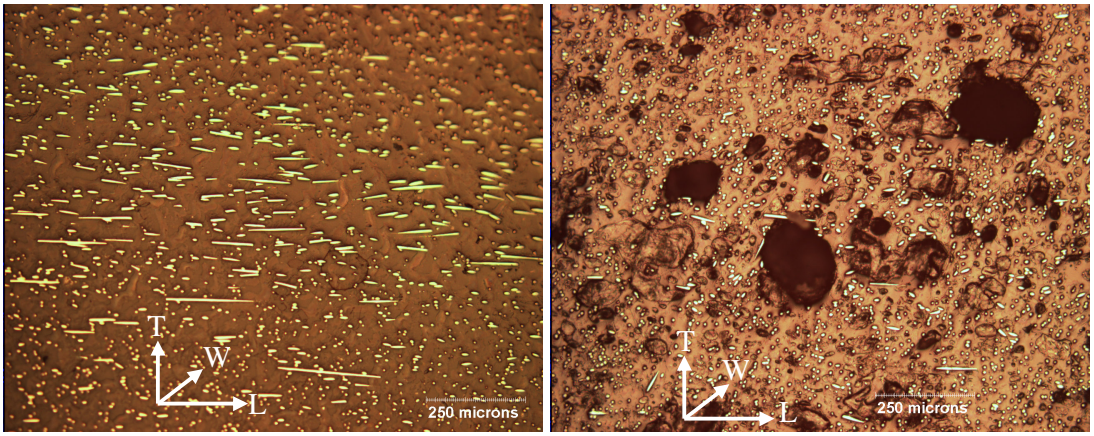

Fig. 4. Micrographs from reflected light microscopy showing the fiber orientation distribution of the injection molded composites: Left: non-foamed sample (A) and Right: foamed sample (C)

Conclusions

The fractional factorial design showed that foaming of COC/CF($10\%_{v/v}$)-CB($2.5\%_{v/v}$) at suitable injection molding conditions can lead to the improvement of electrical conductivity transverse (W) and perpendicular (T) to the flow direction. Further investigation by using pure CBA powder instead of CBA concentrate at a selected injection molding condition showed improved electrical conductivity by more than one order of magnitude in the T direction and several folds in the W direction.

References

1. Papathanasiou, T. D. and Guell, D. C. (1997), “Flow Induced Alignment in Composite Materials”, Woodhead Publishing Limited
2. Weber, Mark and Kamal, Musa R. (1997), *Polym. Eng. Sci.,* Vol. 18, No. 6, pp. 726-740
3. Dani, Ashay A. and Ogale, Amod A. (1996), *Comp. Sci. Tech.*, 56(8), pp. 911-920
4. Yang, Y. and Gupta, M. C. (2005), *Adv. Mater.,* 17, pp. 1999-2003
5. Qin, X., Thompson, M. R. and Hrymak, A. N. (2005), *Polym. Eng. Sci.*, 45 (8), pp. 1108-1118