INJECTION-MOLDABLE COKE-PITCH BLENDS

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Introduction

Injection moldable carbon precursor compounds are of interest for mass production of graphite components. This goal has been achieved using different technological approaches [1, 2]. Most utilize binders that must be removed before carbonization. Instead this study considered the use of PVC, a graphitizable polymer [3] as binder in conjunction with pitch. PVC is also compatible with the pitch. Binder removal after molding is unnecessary as it ultimately becomes part of the final product.

Experimental

The filler was Sasol calcined medium temperature pitch coke (CMTPC). It was milled into a fine powder (mean particle size of 6 µm) in a bead mill. ArcelorMittal pitch with a softening point of 110 °C (110MP) was used as primary binder. PVC was organically stabilized with an organic additive, i.e. Ecostab 6300 supplied by SunAce.

All compositions are reported on a mass basis with X/Y/Z corresponding to the coke/pitch/stabilized PVC content. The formulations are given in Table 1. Granulated compounds were prepared on a 28 mm twin screw laboratory extruder line. Test bars measuring 130 x 14 x 6.5 mm (Fig. 1) were injection molded on an 80 ton ENGEL machine using a Charpy impact mold.

Fig. 1 Image showing injection molded coke pitch PVC test bars.

Raman spectra were recorded on a T64000 series II triple spectrometer system from HORIBA Scientific, Jobin Yvon Technology using the 514.3 nm laser line of a coherent Innova®70 Ar^+ laser. The spectra were recorded in a backscattering configuration with an Olympus microscope attached to the instrument (using a LD 50x objective) at a resolution of 2 cm^{-1} in the range 1200 to 1700 cm^{-1}. A liquid nitrogen-cooled CCD detector was used. The laser power was 6 mW at the sample. The accumulation time was 120 minutes for all samples. The spectra were baseline corrected with LabSpec software program.

Thermo-gravimetric (TG) analysis was performed on a Mettler Toledo A851 simultaneous TG/DTG machine. Samples, ca. 20 mg in size, were placed in 70 µl aluminum crucibles and temperature scanned from room temperature to 1000 °C at a rate of 10 °C/min and a N_2 flow rate of 50 mL/min. The carbon yield was taken as the residue present at the end of the run. The effect of oxygen treatment on carbon yield was studied using the following protocol: Heating in air from 25 °C to 400 °C at 10 °C/min; quench to 25 °C at 100 °C/min; Switch to N_2 and wait 1 min before reheating to 1000 °C at 10 °C/min in N_2 flowing at 50 mL/min.

Melt viscosity was measured using a Göttfert Rheograph 2002 capillary rheometer at 160 °C except for the 0/90/10 wt % composition (T = 120 °C). The capillary die had an L/D of 30/1 and an entrance angle of 180 °.

Electron beam (EB) crosslinking was done on a Budker Institute of Nuclear Physics series ELV machine at the Leibniz-Institute for Polymer Processing in Dresden, Germany. It was operated in the energy range 0.6 MeV to 1.5 MeV. The maximum beam power was 20 kW and the maximum beam current 25 MA. All samples were irradiated under a blanket of oxygen. Doses and dosage rates used are indicated in Table 1.

Molded samples of the 50/45/5 wt % composition were carbonized at 1000 °C for 1 h and graphitized at 2400 °C for 2 h. The following codes were used to identify the different sample stages: IM is green material i.e. injection molded test bars; EB is an electron beam crosslinked green material, and CIM is carbonized IM. GIM and GEB refer to graphitized IM and EB respectively.

Table 1. Electron beam crosslinked coke pitch PVC compounds.

Compositions (wt %)	EB (kGy)	EB rate (kGy/h)
50/45/5	400	10
50/40/10	400	10
0/75/25	400	10
0/50/50	100	3000
0/25/75	100	3000
0/0/100	100	3000

Results and Discussions

Fig. 2 shows Raman spectra of 50/45/5 composition from the green to graphitized material. The carbonized sample shows isotropic behavior since G-band and D-band intensities are similar. IM and EB have I_D/I_G intensity ratios of 0.77 and 0.78 respectively, and their curves are comparable to each other. This is also shown in Fig. 2. The GEB and GIM graphitized samples featured a narrow intense G-band and a small broad D-band indicating a more graphitic nature. Electron beam crosslinking was generally beneficial, showing

sharper G-bands than samples at the corresponding stage that were not crosslinked. GIM and GEB had I_D/I_G intensity ratios of 0.23 and 0.19 respectively. These values compare favorably with the 0.18 intensity ratio for natural graphite.

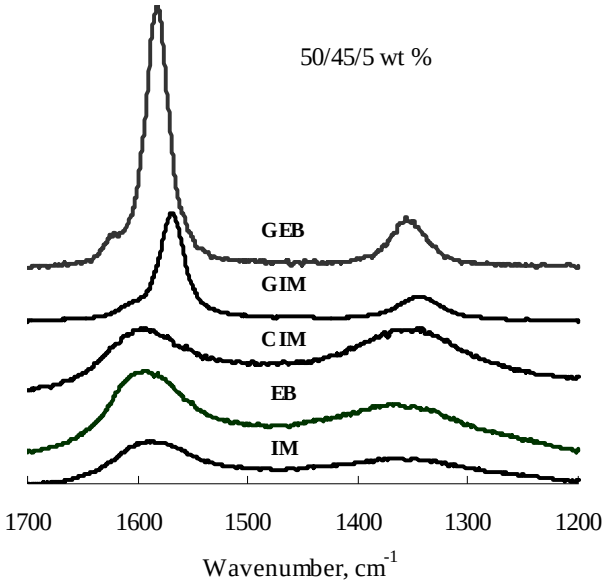

Fig. 2 Raman curves from green to graphitized compound.

Coal tar pitch i.e. 110MP cross-links when exposed to oxygen even at low temperatures [4] (Table 2). Samples heat treated in air and nitrogen protocol showed higher carbon yields. This indicates the benefit of oxygen crosslinking.

Table 2. Carbon yield (TG residual mass at 1000 °C) for green pitch PVC blends.

X/Y/Z (wt %)	Nitrogen (wt %)	Heating Protocol (wt %)
0/100/0	37.6	46.5
0/90/10	36.0	38.6
0/75/25	33.7	33.8
0/50/50	28.1	33.1
0/25/75	20.5	23.9
0/0/100	9.9	11.3

Pitch-PVC blend melts showed strong shear thinning (Fig. 3). The 0/75/25 and 0/50/50 wt % blends showed a slip-stick flow pattern at high shear rates (> 1000 1/s). Similar behavior was observed for the 0/90/10 wt % compound at a shear rate > 100 1/s. The reason for this unexpected behavior is currently unknown.

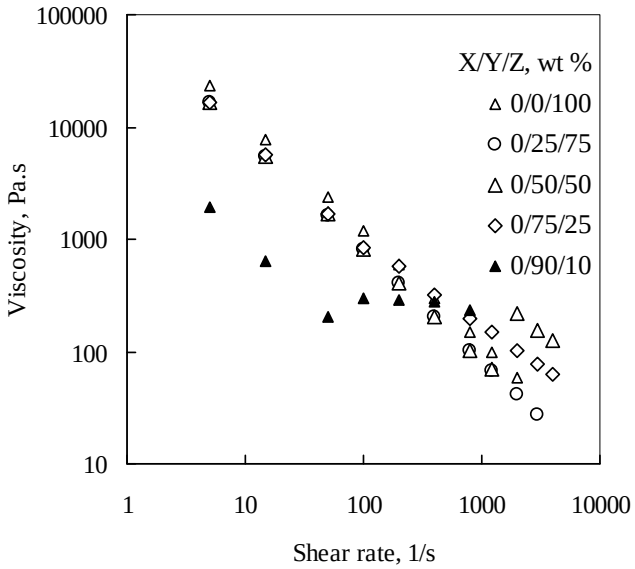

Fig. 3 Viscosity as a function of shear rate pitch-PVC blends.

Conclusions

Injection-moldable PVC-pitch blends containing coke filler particles were prepared by twin-screw extrusion compounding. The melts of these blends showed strong shear thinning behavior. Some exhibited slip-stick flow behavior at high shear rate (> 100 1/s). Oxygen crosslinking improved the carbon yield of pitch PVC blends. Raman spectroscopy indicated a graphitic character for the graphitized 50/45/5 coke/pitch/PVC compound.

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