Magnetic Properties of Pyro-Carbons Prepared from Poly(vinyl chloride) and Activated Carbon

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Synopsis. The magnetic properties of pyro-carbons prepared from poly(vinyl chloride) and activated carbon were examined. In contrast with the observation of a hysteresis from vibrating sample magnetometer measurement, the ESR spectra showed only an usual $\Delta m_s=\pm 1$ signal. The temperature dependence of the magnetic susceptibility approximately obeys Curie's law: The estimated spin density is ca. 10^{19} spins/g, roughly close to that calculated from ESR method. Therefore, it seems likely that the bulk magnetic nature of PVC/C sample is still paramagnetic, although there is a possibility that local microregions having anomalous high spin character could be formed in the sample.

Much attention has been paied to magnetic properties of organic compounds.[1-5] Of these, substances pyrolyzed at the temperature of ca. 1000 °C could be one of the compounds suitable for investigating their magnetic properties because there would be a lot of unpaired electrons in an incomplete graphite structure.[5] In the course of our works on partial graphitization, we found that there is some difference in the addition effect of activated carbon on the magnetic properties between a graphitizable poly(vinyl chloride) (PVC) and non-graphitizable cyclic tetramers of resorcinol and aldehyde. From this clue, we have already confirmed[6] that the magnetic nature of these pyro-polymers would come from a carbon structure itself[7] but not metal impurities.[8] However, it is still not clear whether the observed magnetic properties are a pure ferromagnetic state or only a locally ordered spin state.[9] In this paper, the results of the magnetic susceptibility measurements are briefly reported together with the vibrating sample magnetometer (VSM) and electron spin resonance (ESR) analyses.

Experimental

Pyro-carbons (PVC/C) from PVC and activated carbon were prepared at 1000 °C under argon stream according to the procedure previously reported.[6b] The magnetic properties of the samples were recorded on a VSM model TM-VSM1550HGC (Tamagawa-seisakusho Co., Ltd.) and a model HSM-2000 SQUID susceptometer (HOXAN). The ESR spectra were measured with a JEOL JES-RE1X spectrometer: The samples were sealed in 5 mm-o.d. quartz tubes under vacuum. The transition metal impurities were determined by ICP spectrometer (Shimadzu ICPV-1000).

Results and Discussion

The PVC/C sample when floating on water surface in a Petri dish responded to the field of a permanent magnet (NEOMAX ca. 6 kG). The lattice spacing (d), being calculated from the X-ray diffraction profile of (002) lines of near $2\theta=25°$ of the sample, is 3.62 Å, larger than that of graphite (3.35 Å).[10] The electrical conductivity of the sample, measured by a dc four-probe method using silver paste, was 10 S cm^{-1}.

The ESR spectra showed only an usual $\Delta m_s=\pm 1$ signal, being a Dysonian-shape without hyperfine structures (Fig. 1); no forbidden $\Delta m_s=\pm 2$ signal was observed even at 77 K.[11] The ESR data are given in Table 1. The g-value for the $\Delta m_s=\pm 1$ signal suggests that the spins are ascribed to carbon. The ΔH_{pp} and the g-value of PVC/C sample are close to those of alkylene-aromatic ($\Delta H_{pp}=4.24$ G, $g=2.0029$)[11] and electrically conducting polymers ($\Delta H_{pp}=6.53$ G, $g=2.0024$ for poly(3-methylthiophene[12]).

The VSM data of the sample at room temperature showed a hysteresis loop (Fig. 2). An apparent saturation magnetization (M_{app}) was ca. 0.27 emu g^{-1} and the coercive force (H_c) was 63 Oe ((1 Oe$=10^3(4\pi)^{-1}$ Am^{-1}). The ICP analyses showed that no Co and Ni metals existed and Fe metal content was less than 30 ppm. The observed M_{app} value is equivalent to about 1200 ppm Fe, at least about 40 times greater than that of ICP analysis.

The temperature dependence of the magnetic susceptibility (χ) was measured using SQUID susceptometer (Fig. 3). It is found that a possible linear relation between $1/\chi$ and temperature was observed, passing through the origin ($\chi=c/T$, c: Curie constant). Assuming $S=1/2$, the estimated spin density (N_c) is calculated as 7.5×10^{19} spins g^{-1}, roughly close to that calculated from ESR method (Table 1). That the observed χ

Table 1. ESR and SQUID Data

	ESR[a]			SQUID	
	ΔH_{pp} (Gauss)	g-Value	N_s[b] (spins g^{-1})	C[c] (emu K g^{-1})	N_c[d] (spins g^{-1})
PVC/C	5.25	2.0022	4.9×10^{18}	4.66×10^{-5}	7.8×10^{19}

a) At room temperature. b) Curie-type spin concentration. c) The Curie constant. d) Spin concentration.

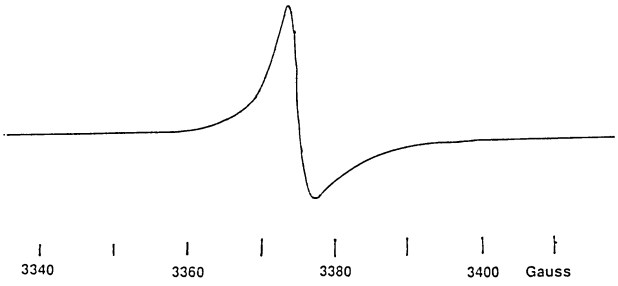

Fig. 1. ESR spectrum of PVC/C sample at room temperature.

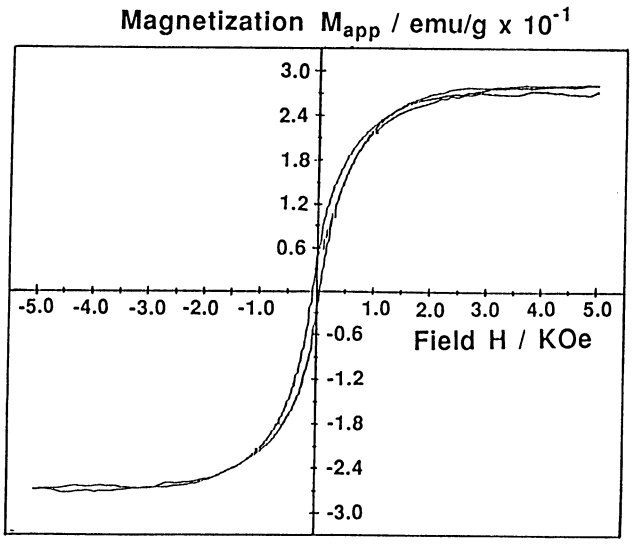

Fig. 2. Field dependence of the magnetization of PVC/C sample at room temperature.

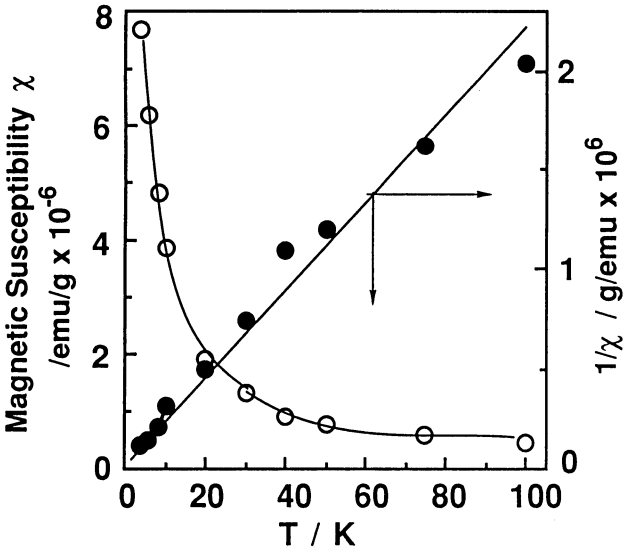

Fig. 3. Temperature dependence of the magnetic susceptibility of PVC/C sample.

value approximately obeys the Curie's law

$$c=\frac{N}{3k}S(S+1)g^2\beta^2$$

could be illustrative of a paramagnet.[13] Considering only paramagnetic ESR spectra with no hyperfine splitting (Fig. 1), it seems likely that a major portion of the sample is still paramagnetic, although there might be unusual high spin microregions in small portions of the sample, since an apparent hysteresis loop was observed from VSM measurements (Fig. 2). Further work will be underway in order to enhance these anomalous regions.

In conclusion, the bulk magnetic nature of PVC/C sample is still paramagnetic. However, there is a possibility that local microregions having anomalous high spin character could be formed in the sample.

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