Changes of structure and magnetization with thermal decomposition and carbonization of aromatic polyimide films

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Introduction

Some organic compounds are excellent in strength and electric insulation, and have high heat-resistant nature. Especially, aromatic polyimides are known to be super heat resistant polymers with high electric resistance [1]. Recently, researches to obtain organic compounds having magnetic properties, such as high spin and ferromagnetism, are performed [2]. We investigated the change in magnetization of aromatic polyimide Kapton (PMDA/ODA) by heat treatment, and found a high spin (total effective spin S=5/2) and ferromagnetism at temperatures close to its thermal decomposition temperature [3,4]. However study of magnetic properties on other aromatic polyimides was scarcely made, though there have been obtained many kinds of polyimides with different molecular structures [1]. In this research, aromatic polyimide films PPT (PMDA/[PPD+TAB]), PMDA/PPD and NOVAX (PMDA/[ODA+OTD]) were heat-treated and changes of the structure and magnetization by heat treatment were investigated. The chemical structure of PMDA/PPD and that of NOVAX are shown in Fig. 1. In the case of PPT, TBA is added as a molar ratio of PMDA/PPD/TAB being 100/92/4. The molar ratio of PMDA/ODA/OTD on NOVA is 100/50/50. The films are high heat-resistant polymers, and PPT is more rigid than NOVAX.

Experimental

PPT with 40 and 30 μm in thickness, PMDA/PPD with 25 μm thick in average and NOVAX with 75 μm thick were used in this study. Each polyimide film was sandwiched between artificial graphite plates, and then put into an infrared furnace. The films were heated under nitrogen atmosphere in the furnace with a heating rate of 2 K/min, and kept for 1 h at each required temperature. For the heat-treated films, X-ray diffraction (XRD) and FT-IR measurements were carried out. Magnetization measurements using a SUQID magnetometer were also performed. Field dependence of magnetization at temperatures of 300 and 5 K and temperature dependence of magnetization in a field of 1 T were made. Total effective spin S and number of magnetic moment per kg N were determined from the results of magnetization data using the Brillouin function.

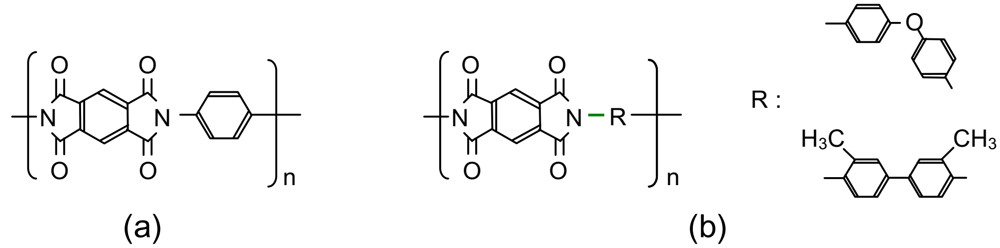

Fig. 1. Chemical structure of (a) PPT (PMDA/PPD) and (b) NOVAX (PMDA/ODA+OTD).

Results and Discussion

The results of XRD on transmission mode are shown in Fig. 2 for the original and heat-treated films of PPT with 40 μm thick, PMDA/PPD with 25 μm thick and NOVAX with 75 μm thick. PPT and PMDA/PPD are found to be very similar crystal structure according to the XRD diffraction patterns. It was suggested that crystallinity of PPT and PMDA/PPD are better than that of NOVAX. Crystal structure was lost by heat treatment above about 550 °C in PPT and PMDA/PPD, and about 480 °C in NOVAX.

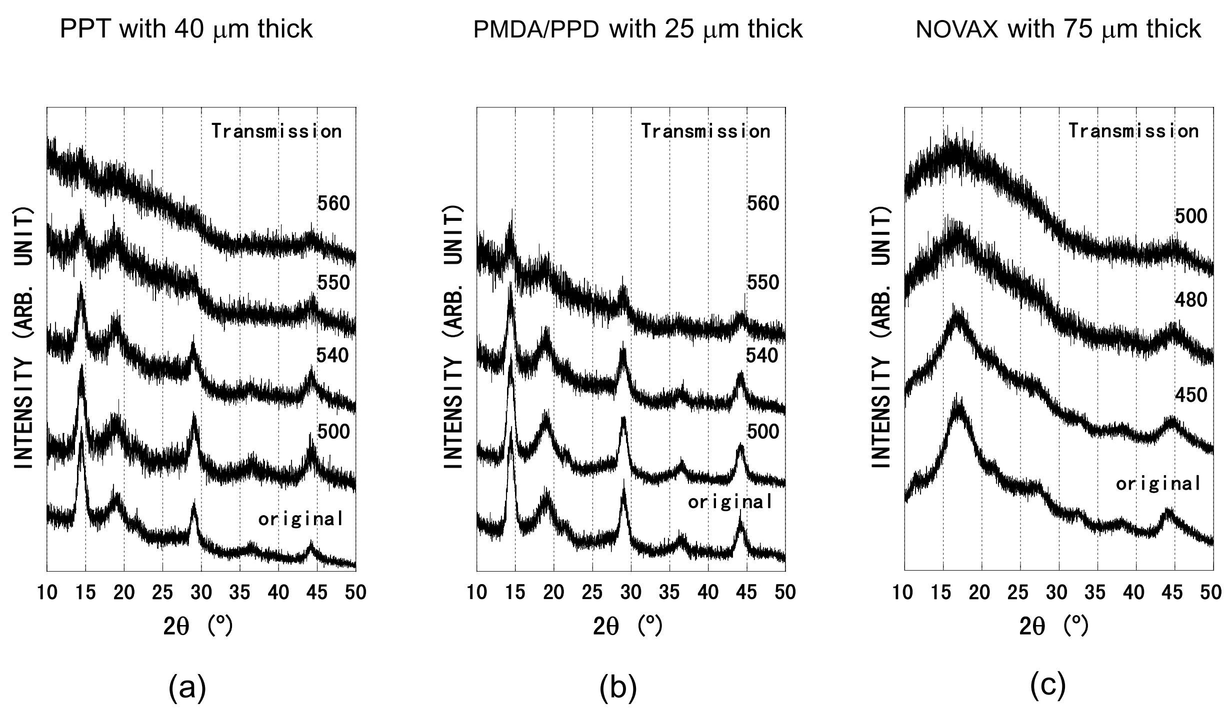

Fig. 2. X-ray diffraction patterns on transmission mode for (a) PPT with 40 μm thick and heat-treated films, (b) PMDA/PPD with 25 μm thick and heat-treated films and (c) NOVAX with 75 μm thick and heat-treated films.

As shown in Fig. 3, the absorbance of FT-IR spectrum attenuates from around a heat treatment temperature (HTT) of 550°C for PPT. The result agrees well with that of the structural change of PPT obtained by XRD. On the other hand, the absorbance decreases partially on 1500, 1200, 1100 and 800 cm^{-1} around an HTT of 480°C for NOVAX, corresponding to the structural change of it observed by XRD.

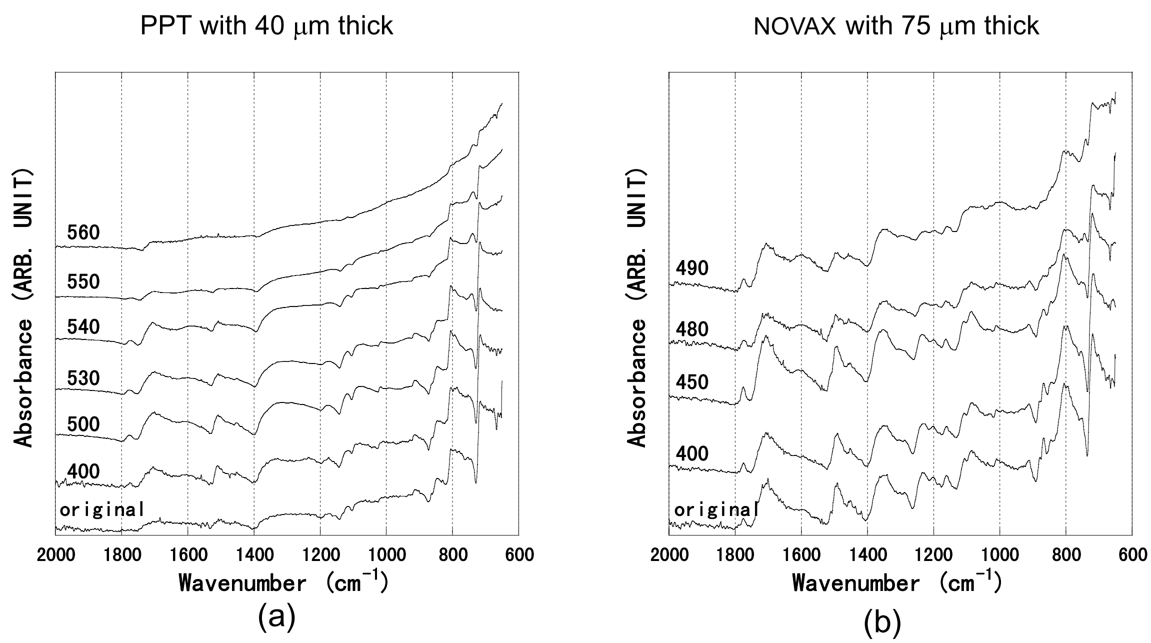

Fig. 3. FT-IR spectra for (a) PPT with 40 μm thick and heat-treated films and (b) NOVAX with 75 μm thick and heat-treated films.

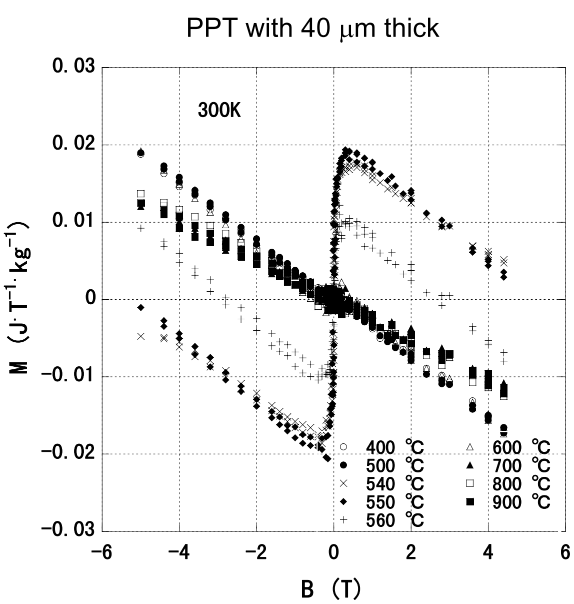

Fig. 4. Field dependence of mass magnetization M at 300K for PPT with 40μm thick and heat-treated films.

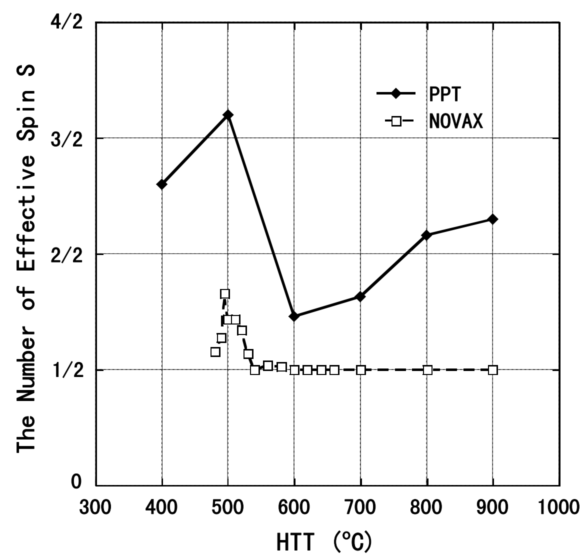

Fig. 5. Total effective spin S as a function of HTT for heat-treated PPT and NOVAX films.

As shown in Fig. 4, ferromagnetism was observed for the 540, 550 and 560°C-treated films at room temperature (300 K). The 500°C-treated film of PPT exhibited a high spin (S~3/2) as shown in Fig. 5. On the other hand, the heat-treated NOVAX films showed no high spin and ferromagnetism. The high spin should be related to an appearance of ferromagnetism. The S value for PPT and NOVAX reaches to the maximum in early stage of thermal decomposition, and the high spin is supposed to be due to spin-spin interactions among the unpaired electrons generated by thermal decomposition. The value of S decreased with the increase of HTT, and the results indicate that the high spin condition is closely related to the existence of crystal structure.

As shown in Fig. 6, the value of N increases with HTT, passes through a maximum and then decreases. The increase of N corresponds to generation of the unpaired electrons by thermal decomposition, while the decrease of N corresponds to the decrease of the unpaired electrons by forming benzene rings. The maximum was observed at HTT of 600°C for PPT, and 640°C for NOVAX, respectively. The 002 x-ray diffraction of carbon layers was observed at HTT's above the HTT giving the maximum.

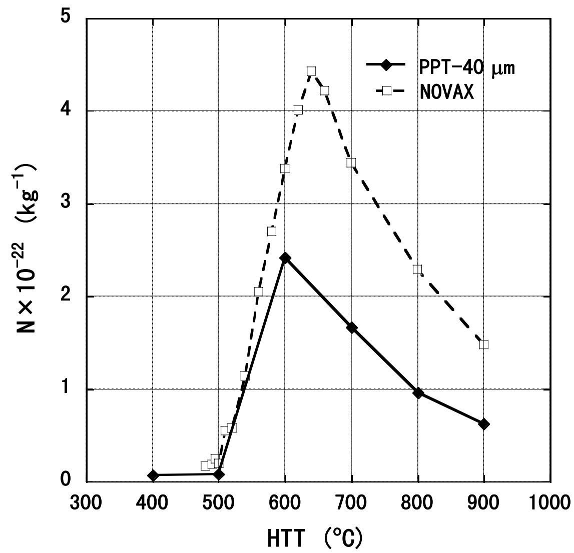

Fig. 6. The number of magnetic moment per kg N as a function of HTT for heat-treated PPT and NOVAX films.

The magnetization measurements were carried out only for 500, 530, 550°C-treated films of PMDA/PPD because high spin condition and ferromagnetism were observed in this HTT range for PPT with 40 μm thick. In the case of PPT with 30 μm in thickness, denoted hereafter PPT-30, the magnetization measurements were also carried out for the films heat-treated in this HTT range. Values of S for the 500, 530, 550°C-treated films of PMDA/PPD and PPT-30 are listed in Table 1. The heat-treated films of PMDA/PPD exhibit no high spin condition and ferromagnetism. On the other hand, the 500°C-treated PPT-30 shows high spin. The S value of 1.8 is very close to S=1.6 for PPT, but ferromagnetism did not observed for the heat-treated PPT-30. The results suggest that TBA influences the spin-spin interactions.

Conclusions

1) Ferromagnetism was only observed for PPT with 40 μm in thickness heat-treated at temperatures between 540 and 560 °C.
2) Total effective spin S reaches to a maximum in the early stage of thermal

decomposition of each film.

3) The high spin was obtained for PPT with 40 μm in thickness heat-treated at 500°C and PPT with 30 μm in thickness heat-treated at 500, 530 and 550 °C.
4) Above results are consistent with those obtained for Kapton previously.
5) Ferromagnetism has been observed at a narrow range of HTT for only limited aromatic polyimide films exhibiting a high spin.

Table. 1. Total effective spin S for hear-treated films of PPT-40 μm, PMDA/PPD and PPT-30 μm.

HTT \ Sample	PPT - 40μm	PMDA/PPD	PPT - 30μm
500	1.6	0.5	1.8
530	-	0.8	1.2
550	-	0.6	1.0

References

[1] Inagaki M, Takeichi T, Hishiyama Y and Oberlin A. High quality graphite films produced from aromatic polyimides. In Thrower PA, Radovic LR., editor. Chemistry and Physics of Carbon, Vol. 26, New York, Marcel Dekker, 1999: 246-333.
[2] Veciana J, Iwamura H. Organic magnets. MRS Bulletin 2000;25(11): 41-51.
[3] Kaburagi Y, Wakabayashi H, Natori S, Toriyama T, HishiyamaY, Utsunomiya M, Tanabe Y and Yasuda E. Change of magnetic property in carbonization processes of Kapton and furan resin. Extended abstracts, Eurocarbon2000 Berlin (Germany) Deutsche Keramische Gesellschaft e. V., 2000;193-194.
[4] Kaburagi Y, Hishiyama Y. Ferromagnetism discovered on heat-treating the aromatic polyimide film Kapton. J. Mater. Res. 2002; 17(8): 2000-2006.