Application of Carbon Nanotube (CNT) to Photosensitive Diazo /PVA Resist

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Degradation temperature, D.T. of the para-substituted benzene diazo compound (SBD) incorporated with multi-walled carbon nanotube (CNT), was determined by TDA and DTA in solid. The D.T. of SBD with CNT was higher than that of SBD with C₆₀, which was higher than that without CNT or C₆₀. Stabilization energies of diazo compounds with CNT (1:1) and C₆₀ (1:1) were calculated to be ~ 57 and ~ 7 kJ/mol by WinMOPAC, respectively. Calculation results support the stability of diazo with CNT or C₆₀. Photodecomposition rate of PVA resist films containing diphenyl-4-diazonium sulfate salts/ formaldehyde condensate (DSR) with CNT was higher than that without CNT. It is considered DSR/PVA with CNT was photo-decomposed reductively and accelerated with the electrons evolved from CNT, absorbing light energy. Hardness of resist layers containing CNT (1/1 to diazo by weight) was larger than that with C₆₀, which was larger than that without CNT or C₆₀. High durability is assumed to be caused by compact packing of the polymer chains with nanocarbons.

Keywords: photosensitive diazo compound, multi-walled nanotube (CNT), C₆₀, thermal decomposition, hardness

1. Introduction

The para-substituted benzene diazo compounds (SBD) with electron-donating (DSBD) are used as photo acid generators for micro resists [1], photosensitive emulsions for the screen printing resist [2], and UV-fixable thermal recording papers [3-5]. SBD with electron-withdrawing substituents (WSBD) was used for acid generators for polymerization. 18-Crown-6 (18C6) complexes with benzene diazonium cation improve photo and thermal stability of diazo compounds [6-9]. Thermal decomposition of less expensive β-cyclodextrin (CD) complex with diphenylamine-4-diazonium sulfate/ formaldehyde condensate/PVA resist (DSR-PVA) was suppressed[10-12]. The coloring of the DSR/PVA emulsion films was suppressed by inclusion of 18C6 or PEG [10].

Previously we reported [13] on the effects of C₆₀ applied to a diazo/PVA resist. The degradation temperature, D.T., and stabilization energy of SBD with C₆₀ were higher and hardness of SBD with C₆₀ was larger than that without C₆₀. There are many reports on application of single-walled carbon nanotubes to electronic devices [14,15]. In this study, multi-walled carbon nanotube (CNT) which was used for the lower price, instead of the single-walled nanotube, was evaluated for degradation temperature, D.T., and hardness of a diazo compound and a diazo/PVA resist.

2. Method

2.1 Materials

p-Substituted benzene diazonium tetrafluoroborates (SBD) were precipitated by adding hydrogen tetrafluoroborate to an aqueous solution of the corresponding benzene diazonium chloride prepared from p-substituted aniline. The solid product was recrystallized from ethanol. The conventional photosensitive diazo resin, DSR and PVA emulsion for screen printing, were purchased from Murakami
Screen KK. The additives used were \( C_{60} \) from Aldrich Co., Ltd. and the multi-walled carbon nanotube (CNT) with diameter of 20-30 nm from Microphase Co., Ltd., which was the lower price, instead of the single-walled nanotubes.

Solid for thermal analysis was formed in the following: SBD was mixed with CNT or \( C_{60} \) powders. Coating solutions of the resist were prepared by dissolving 0.6g of the diazo compound in 100g of the matrix PVA-emulsion in water together with the additives. The resist layers (PVA films) for photodecomposition and hardness were coated onto glass plates to a thickness of 15.3 μm and screen clothes to a thickness of 25 μm, respectively. UV spectra of the films were measured with a Shimadzu UV-1600 PC spectrophotometer.

2.2 Measurements

The degradation temperature (D.T.) was determined by TDA and TGA measured with a Shimadzu ETG-60 Analyzer. Resist layer (PVA films) were irradiated by a Sunhatoya Chibi Light Model BOX 1 with fluorescence light (FL-6BL). The incident energy was 2.2mW/cm\(^2\). Hardness of films were measured by a Nishitokyo WR-105 Hardness Meter.

2.3 Computational experiment

Calculation was performed with WinMOPAC ver. 3.5.1a (served by Fujitsu Co. Ltd.) in a personal computer [16]. The EF routine and MOZYME [16] routine were used for optimizer. The heat of formation (kJ/mol) calculated using the PM5 Hamiltonian. For other parameters default values programmed in MOPAC2002 were used.

3. Results and Discussion

3.1 Degradation temperature of solid complex

Degradation temperature, D.T. of SBD with \( C_{60} \), or CNT was determined by DTA and TGA measured in solid state. Hammett plots of D.T. in solid state were shown in Fig.1. The D.T.s of SBD with CNT was higher than that with \( C_{60} \). A cationic diazo group of SBD is easily coordinated the electron rich CNT.

3.2 Estimation of the stabilization energies of diazo-compound with CNT by WinMOPAC calculation

Optimized structures and the heat of complex-formation of CNT, \( C_{60} \), benzene diazonium cation (BD) with CNT or \( C_{60} \) were calculated by WinMOPAC.
Optimized structures of BD with CNT (1:1) and with C₆₀ (1:1) are shown in Fig.2. Calculated heat of formation of BD, CNT, C₆₀, and BD complexes with CNT (1:1) and C₆₀ (1:1) were 1038, 2091, 3394, 3071, 4425 [13], kJ/mol, respectively. Estimated stabilization energies of BD with C₆₀ (1:1) and CNT (1:1) were −7 [13] and -57 kJ/mol, respectively as shown in Fig.3. The latter was larger than the former of D.T. stated.

Stabilization energy of BD with CNT was larger than that with C₆₀. Calculation results support the stability of BD with CNT or C₆₀ by experimental data of D.T. stated in 3.1.

3.3 Photodecomposition of DSR/PVA resist with CNT or C₆₀

The residual DSR with CNT or C₆₀ in DSR/PVA film after UV irradiation were measured by UV spectrometry and the remaining weight of diazo compounds (%) calculated. The constitution of DSR/PVA resist with CNA will be shown as Scheme 2. Photodecomposition rate of DSR/PVA resist with CNT was a little higher than that without CNT. It is considered that DSR/PVA with CNT was photo-decomposed reductively and accelerated by evolved electrons from CNT absorbed light energy.

3.4 Hardness of resist

Diazo/PVA resist layers containing CNT or C₆₀ was washed with water after irradiation, and dried. Hardness of resist layers with CNT (1/10 ~ 1/1 to diazo by weight) was larger than that with C₆₀, which was larger than that without additives.
4. Conclusion

When CNT applied to photosensitive diazo compounds, the shelf life of diazo compounds was improved. DSR/PVA resist with CNT is improved in thermal stability and photo-sensitivity. Hardness of CNT-containing DSR/PVA resist was found to increase, which may be closely related to high durability caused by compact packing of the polymer chain with long CNT.

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References