Poly(1,3-propylene glycol-hexanedioic acid) Grafted Hydroxyl Multiwall Carbon Nanotubes

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ABSTRACT: Poly(1,3-propylene glycol-hexanedioic acid) grafted hydroxyl multiwall carbon nanotube (PHHCNT) was fabricated in the presence of butyl titanate using 1,3-propylene glycol, hexanedioic acid, and hydroxyl multiwall carbon nanotubes as reactants. The hydroxyl groups at carbon nanotubes reacted with hexanedioic acid and a small amount of carboxyl groups reacted with 1,3-propylene glycol, resulting in the PGHA grafted on the carbon nanotubes. The carbon nanotubes surrounded by the PGHA chains with an average thickness of ∼ 2 nm. The polycondensation reactions can be controlled by the feed contents of HCNTs and the catalyst concentration in the reactants. The content of HCNTs in PHHCNT rises with an increase of the feed contents of HCNTs. In addition, the content of HCNTs in PHHCNT is higher than the feed contents of HCNTs in the reactants. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2018–2024, 2007

Key words: graft copolymers; polyesters; structure-property relations; synthesis

INTRODUCTION

Carbon nanotubes (CNTs) are undoubtedly one of the most outstanding discoveries in the chemistry and materials fields.[1] The unique properties of CNTs make them possess wide applications, including the high-strength composites,[2] conducting and semiconducting materials,[3,4] energy storage devices,[5] electromechanical actuators, and so on. Their realistic applications in materials and devices have been hindered by the poor compatibility with matrix. The early CNTs composites were prepared by physically mixing multiwalled carbon nanotubes (MWNTs) with polymers.[6] CNTs are easily drawn out from matrix because of the weak interaction between polymers and the surfaces of the CNTs. Several methods, i.e., solution casting,[7,8] electro-spinning,[9,10] *in situ* polymerization,[11–13] and surfactant-assisted processing of CNTs-polymer composites,[14] have been developed for the fabrications of CNTs-polymer composites to improve the interaction force between CNTs and matrix.

A novel method to make CNTs and aliphatic polyester in a compatible fashion was designed by the esterification of the surface-bound hydroxyl groups of HCNTs with PGHA. The composition and structures of the product were studied. This product can potentially be used as plasticizing agents for CNTs/polymer hybrid systems to improve the compatibility between CNTs and polymers.

EXPERIMENTAL

Materials

HCNTs were purchased from Institute of Organic Chemistry in Chengdu of Chinese Academy of Sciences (Chengdu, China). They were prepared by acid treatment of CNTs that were produced by the arc-discharge method. HCNTs contain ∼ 3–4% hydroxyl groups according to the product description. HCNTs were curved and coiled [Fig. 1(a)], with 5–10 nm in internal diameter, 10–20 nm in external diameter, 0.5–500 μm in length, and 10–30 graphite layers. HCNTs were partially oxidized [Fig. 1(b–d)].

1,3-propylene glycol (Analytical Reagent, A. R.), hexanedioic acid (A. R.), butyl titanate (A. R.), triphenyl phosphite (A. R.) and acetone (A. R.), etc. were obtained from Development Center of Chemical Agent in Tianjin and were used without further purification.

Fabrication of PHHCNT

In a typical experimental procedure, 40.6 mL 1,3-propylene glycol, 60 g hexanedioic acids, and a prede-
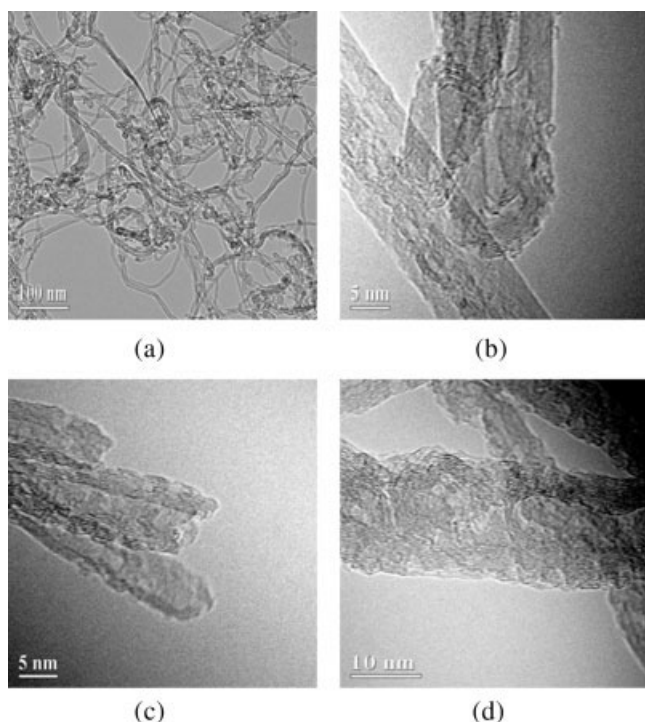
Figure 1 TEM micrographs of (a) HCNTs by low-resolution, (b) HCNTs by high-resolution, (c) open ends, and (d) sidewalls of HCNTs.

termined mass of HCNTs were mixed in a 250 mL three-necked flask in oil bath at 180–200°C, stirred and refluxed for about 4 h, followed by removal of produced water. Then a predetermined volume of butyl titanate (catalyst) and 4 ∼ 5 drops of triphenyl phosphite (heat stabilizer) were added through transfer pipette to the reaction systems. The mixture was stirred continuously for 2 h, and then was vacuum distilled till no fraction was produced. The yield water and the excess acid left per hour (acid number) were measured. The products were cooled at room temperature. They were washed with acetone for several times to remove unattached

poly(1,3-propylene glycol-hexanedioic acid (PGHA) and monomers since acetone is a good solvent of 1,3-propylene glycol, hexanedioic acid, and PGHA. The residue was dried in a oven at 50°C till its weight kept as a constant. PHHCNT was obtained as grayish black powder. The fabrication process of PHHCNT is shown in Figure 2.

The feed volume or weights of every reactant are listed in Table I.

Calculation

The extents of reaction (P) were estimated by calculation of acid numbers (A), which was the excess acid left per hour in reaction system. The intermediate product was analyzed per hour. It was dissolved in 15 mL solution of ethanol and toluene with a volume ratio of 1 : 1 so as to be quantified. The solution was calibrated by $0.1M$ standard KOH.

$$P = (A_1 - A_2)/A_1 \qquad (1)$$

$$A = (V \times N \times 0.056 \times 1000)/g \qquad (2)$$

where, A_1, initial acid number; A_2, acid number per hour (mg KOH/g product); V, the titrimetric volume of KOH; N, the mol concentration of KOH; g, the mass of intermediate product.

The number of functional group of HCNT was estimated by TGA plot of PHHCNT. The weight loss of HCNTs was 11.3 wt % in the TGA process in the range of 50–1000°C. By contrast, the weight loss of CNTs was 4.3 wt % in the same temperature range. The difference of weight loss between HCNTs and CNTs is 7.0 wt %. The functional group density of HCNTs, estimated from this difference of weight loss, is ∼ 4.12 mmol/g of HCNTs, 4.43 mmol/g of neat CNTs, or ∼ 5.3 functional groups per 100 carbons.[12] It is higher than 3–4% hydroxyl groups given by the producer since there are inevitable some carboxyl groups on HCNTs.
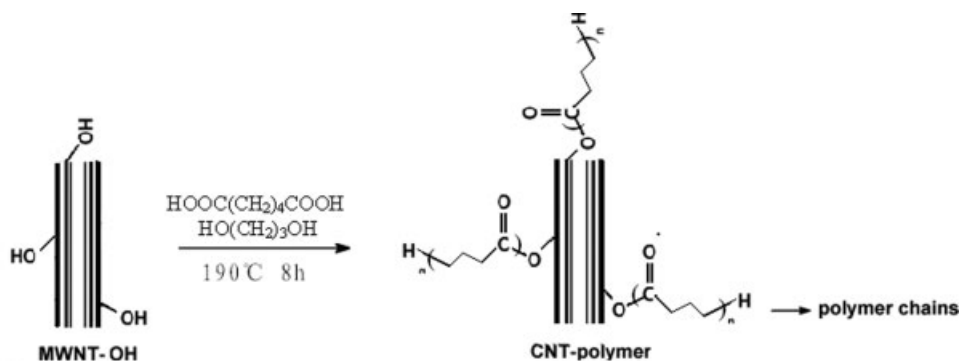

Figure 2 Schematic figure of fabrication process of PHHCNT.

TABLE I
Feed Volume or Weight of Every Reactant

Sample no.	Feed volume or weights				
	1,3-Propylene glycol (mL)	Hexanedioic acids (g)	HCNTs (mg)	Butyl titanate (mL)	Feed contents of HCNTs (wt %)
0	40.6	60	0	0.6	0
1	40.6	60	103.2	0.6	0.1
2	40.6	60	516.0	0.6	0.5
3	40.6	60	1032.0	0.6	1
4	40.6	60	3096.0	0.6	3
5	40.6	60	5160.0	0.6	5
6	40.6	60	103.2	0	0.1
7	40.6	60	103.2	0.2	0.1
8	40.6	60	103.2	1.0	0.1
9	40.6	60	103.2	2.0	0.1

Characterization

Transmission electron microscopy (TEM) analyses were conducted on a Philips Tancnai F20 system with a field emission source. The accelerating voltage was 20 kV. PHHCNT suspension was prepared by ultrasonic and a drop of suspension was placed on a copper grid. The samples were observed after drying at room temperature.

Thermogravimetric analysis (TGA) was performed with NETZSCH STA409 PC/PG TG-DTA thermal analyzer system under nitrogen atmosphere at a heating rate of 10°C/min.

Fourier transformed infrared (FTIR) spectra of the samples were recorded on a VECTOR22 FTIR spectrometer using liquid film method.
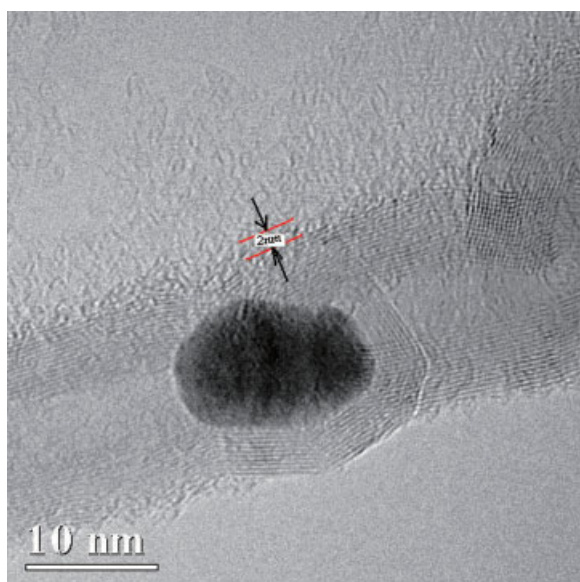
RESULTS AND DISCUSSION

TEM observation

Figure 3(a) shows the TEM micrographs of PHHCNT. It can be found that some parts of the carbon nanotubes are covered with PGHA layer. The PGHA layer coated on HCNTs is uneven, and its average thickness is ~ 2 nm. It is thicker than 1.0–1.5 nm reported by Sinani et al.[15]

FTIR spectra

The representative FTIR spectra of PHHCNT are shown in Figure 4. The peak at 3445 cm^{-1} in the spectrum of HCNTs [Fig. 4(a)] is attributed to the hydroxyl bonds. The mass of HCNTs added to the KBr disk is less than the amount required for normal FTIR detection since HCNTs absorbs the infrared rays. Therefore, only a very weak peak, which is assigned to O—H stretch, can be found in the spectrum of HCNTs.
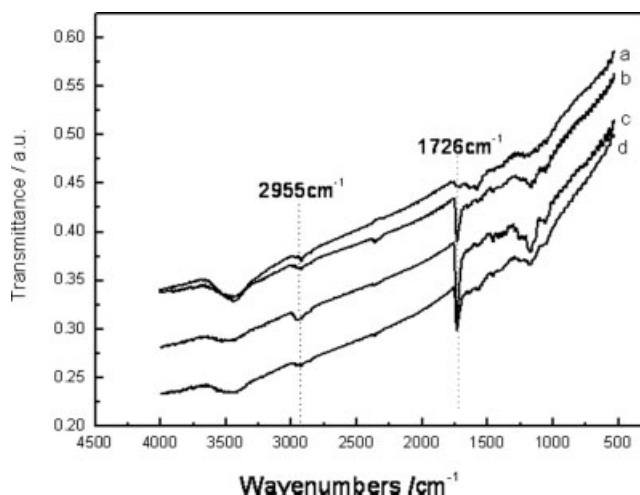

Figure 3 TEM micrographs of PHHCNT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 FTIR spectra: (a) HCNTs, (b) Sample No. 3, (c) Sample No. 4, and (d) Sample No. 5.
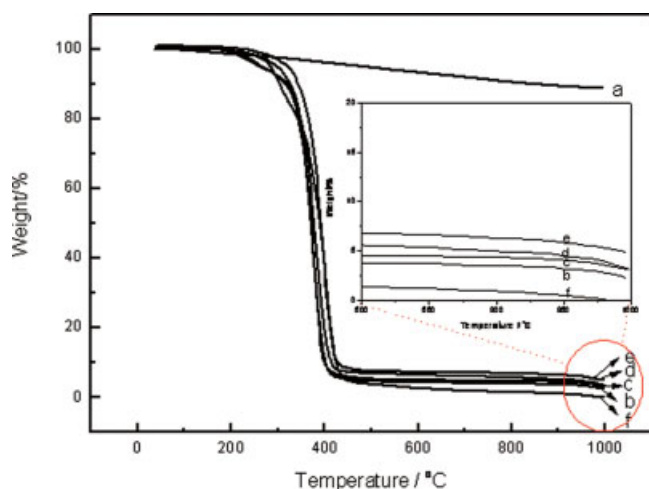
Figure 5 TGA plots: (a) HCNTs, (b) Sample No. 2, (c) Sample No. 3, (d) Sample No. 4, (e) Sample No. 5, and (f) Sample No. 0. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

A sharp peak at 1726 cm^{-1} [Fig. 4(b)] corresponds to C=O stretching mode of the ester group. The absorption bands (ca. 1166 cm^{-1}, 1053 cm^{-1}) are assigned to C—O stretch from the ester bonding. The peak at 2955 cm^{-1} is assigned to the C—H stretch of alkyl portions. As the residue is thoroughly washed with acetone several times and dried under vacuum, the presence of carboxylic absorbance is related to the occurrence of the grafting reaction between PGHA and HCNTs.[16]

In the research on polyethylene glycol and polystyrene grafted carboxylic multiwall carbon nanotubes, both polymer grafted MWNTs and nonfunctional polymer are found in the soluble portion extracted in solvent. The nonfunctional polymer is removed by washing the mixture with the solvent of nonfunctional polymer. Since a few percent of polymer adsorbed on the surface of MWNTs cannot be removed by the washing procedure,[17] the residue in this work probably contains a small portion of non-

functional PGHA. The nonfunctional PGHA content in PHHCNT is very low, since the feed content of HCNTs in the reactants of our experiment is lower than 5 wt %. The MWNTs can absorb 5–50 wt % nonfunctional polymer.[16]

TGA measurement

TGA plot of PHHCNT is shown in Figure 5. Decomposition temperature (T_d), weight loss and the contents of HCNTs in PHHCNT with various feed contents of HCNTs are listed in Table II. Sample No. 0 (pure PGHA) starts to degrade at 202°C, and a weight loss of 99.6% is observed at the curve. Samples No. 2 and 5 begin to decompose at 219°C and 266°C, respectively. The weight loss of PHHCNT decreases from 94.1 to 91.9% with the increase of the feed contents of HCNTs from 0.5 to 5 wt %. Therefore, the thermal stability of PHHCNT sample is improved due to the addition of HCNTs. This result is similar to that of Jung et al.[18]

The content of HCNTs in PHHCNT was measured by TGA. The contents of HCNTs in PHHCNT are listed in Table II. The residue of HCNTs and the PGHA are 88.7 and 0.4 wt %, respectively. The contents of HCNTs in PHHCNTs are 6.2, 7.0, 8.4, and 8.7 wt %, respectively, as the feed contents of HCNTs are 0.5, 1, 3, and 5 wt %, respectively. Most of the nonfunctional PGHA and all of the reactants are removed from PHHCNTs by washing the sample with acetone. Therefore, the contents of HCNTs in PHHCNTs are significantly higher than the feed content of HCNTs.

Supposing that HCNTs absorb 50 wt % nonfunctional PGHA, the content of nonfunctional PGHA in Sample No. 5 is no more than 4.4 wt %. Sample No. 5 is composed of no more than 4.4 wt % of nonfunctional PGHA, ~ 8.7 wt % HCNTs and more than 86.9 wt % of functional PGHA. The ratio of grafted PGHA is ~ 95 wt %. If HCNTs absorb only 5 wt %

TABLE II
Decomposition Temperature (T_d), Weight Loss, the Contents of HCNTs in PHHCNT and the Number of Repeating Unit of PGHA

Sample no.	Feed contents of HCNTs	T_d (°C)	Weight loss (wt %)	Residue weight (wt %)	HCNTs content in PHHCNT (wt %)	Mol of carbon atoms in PHHCNT/ 100g	Mol of Hydroxyl groups in PHHCNT/ 100g	Polymer content in PHHCNT/ 100g	Number-average molecular weight	n
HCNTs	100	–	11.3	88.7	(100)			0		
0	0	210	99.6	0.4	(0)			100		
2	0.5	219	94.1	5.9	6.2	0.52	0.028	93.8	3350	18
3	1	241	93.4	6.6	7.0	0.58	0.031	93.0	3000	16
4	3	222	92.1	7.9	8.4	0.70	0.037	91.6	2475	13
5	5	266	91.9	8.1	8.7	0.73	0.039	91.3	2341	12

TABLE III
Polymerization Conditions and the Extents of Polycondensation Reaction

Sample no.	0	1	2	3	4	5
HCNTs/polyester (wt %)	–	0.1	0.5	1	3	5
Catalyst/polyester (wt %)	0.3	0.3	0.3	0.3	0.3	0.3
Polycondensation time	4	4	4	4	4	4
Vacuum distillation time	2	2	2	2	2	2
Water yield (mL)	11.85	12.10	12.25	12.33	12.70	14.30
Water yield in theory (mL)	14.79	14.79	14.79	14.79	14.79	14.79
The extent of polycondensation reaction by water yield (%)	80.12	81.81	82.83	83.35	85.87	96.69
Initial acid number	373.02	373.02	417.13	646.41	553.02	552.45
Final acid number	7.20	5.15	4.92	5.43	4.20	2.21
The extent of polycondensation reaction by acid number (%)	98.07	98.62	98.82	99.16	99.24	99.30

nonfunctional PGHA, the ratio of grafted PGHA is ∼ 99.5 wt %.

Assuming all of the functional groups on HCNTs react with hexanedioic acid and all of the PGHA chains are grafted on HCNTs, the mean number average molecular weights and the number of repeating unit of grafted PGHA are estimated. The results are listed in Table II. The number average molecular weights ($\overline{M}_n$) of PGHA of Samples No. 2 to 5 are ∼ 3350, 3000, 2475, and 2341, respectively. The numbers of repeating unit (n) of (1,3-propylene glycol-hexanedioic acid) are 18, 16, 13, and 12, respectively, for Sample No. 2–5. It is reasonable that $\overline{M}_n$ and n decrease with the increase of the feed contents of HCNTs. The number of repeating unit decreases with the increase of the number of functional groups at the ends of the polymer chains.

Measurement of the extent of reaction

The extents of polycondensation reaction were measured by titration of the left acid during the reaction. The reaction conditions and test results are summarized in Table III.

The extents of reaction were obtained by titration of acid number in various reaction periods. The effect of the feed contents of HCNTs in reactants on extent of polycondensation reaction is shown in Figure 6. The extents of polycondensation reaction rise with an increase of the feed contents of HCNTs in reactants. It suggests that the extents of reaction are controlled by the content of HCNTs.

Catalyst effect

There is no information about the effect of the feed contents of HCNTs on the extent of polymerization at present. The extents of polymerization are obtained by two measuring methods, titration of the produced acid and water yield during the reaction. We carried out a series of reactions by varying

amounts of catalyst using weight ratio of HCNTs to PGHA as 0.1%. This allowed us to study the effect of the catalyst ratio on the grafting reaction. The experimental conditions and extent of reaction are listed in Table IV.

The extents of reaction of Samples No. 6–9 are higher than the control. The extents of reaction are enhanced as the feed contents of HCNTs increase. In the other experimental conditions, similar phenomena are also observed. It implies that HCNTs enter into the polycondensation reaction.

FTIR spectra of Sample No. 6–9 are shown in Figure 7. The broad band at 1730 cm^{-1} corresponds to the stretching vibration of the C=O group. The relative intensity of the peak gradually rises with an increase in the concentration of catalyst. It indicates that the catalyst enhances the grafting yield of PGHA chains onto HCNTs.

TGA plots of the samples are shown in Figure 8. The decomposition of PGHA at about 400°C rises as the concentration of catalyst increases. The data of
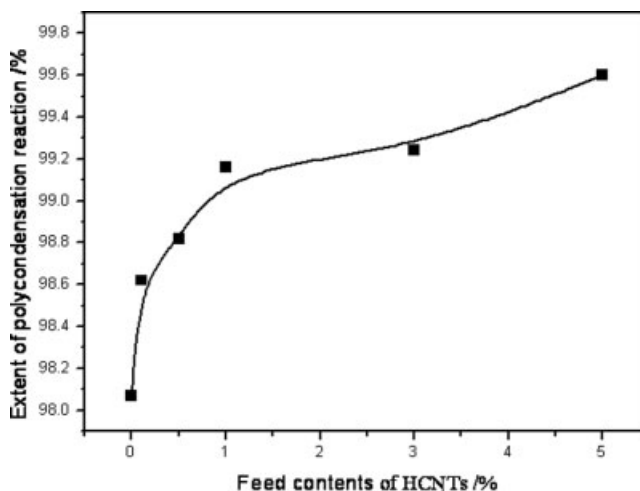

Figure 6 Effect of feed contents of HCNTs in reactants on extent of polycondensation reaction.

TABLE IV
Experimental Conditions and Extent of Reaction

| Sample no.	0	6	7	8	9
HCNTs/polyester (wt %)	–	0.1	0.1	0.1	0.1
Catalyst/polyester (wt %)	0.3	0	0.1	0.5	1
Polycondensation time	4	4	4	4	4
Vacuum distillation time	2	2	2	2	2
Water yield (mL)	11.85	13.00	13.10	13.30	14.50
Water yield in theory (mL)	14.79	14.79	14.79	14.79	14.79
The extent of polycondensation reaction by water yield (%)	80.12	87.89	88.57	89.92	91.95
Initial acid number	373.02	625.10	576.62	620.48	451.89
Final acid number	7.20	10.07	3.92	3.40	0.77
The extent of polycondensation reaction by acid number (%)	98.07	98.39	99.32	99.45	99.83
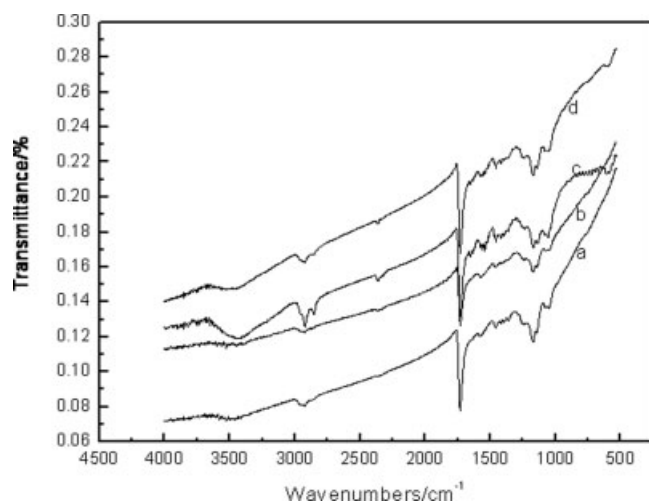
Figure 7 FTIR spectra: (a) Sample No. 6, (b) Sample No. 7, (c) Sample No. 8, and (d) Sample No. 9.
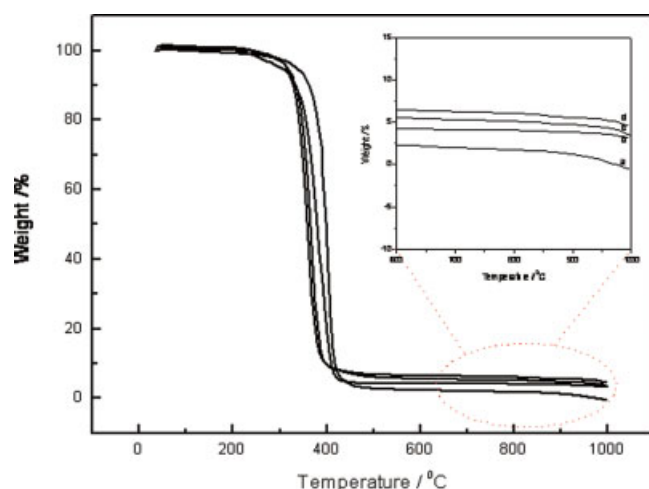

Figure 8 TGA plots: (a) Sample No. 6, (b) Sample No. 7, (c) Sample No. 8, and (d) Sample No. 9. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

weight loss show that the products are primarily composed of the PGHA grafted MWNTs. The weight loss of the products decreases with the increase of the concentration of catalyst. The catalyst can enhance the reactivity of the hydroxyl group on HCNTs. In other words, the reactivity of the hydroxyl group on carbon nanotubes is lower than that in 1,3-propylene glycol.

CONCLUSIONS

Poly(1,3-propylene glycol-hexanedioic acid) grafted hydroxyl multiwall carbon nanotubes (HCNTs) were synthesized in the presence of butyl titanate using 1,3-propylene glycol, hexanedioic acid, and HCNTs as reactants. The PGHA chains were bonded to the surface of hydroxyl multiwall carbon nanotubes by esterification. The PGHA is unevenly coated on the surface of HCNTs. The average thickness of the PGHA layer is about 2 nm. The content of HCNTs in PHHCNT rises with the increase of the feed contents of HCNTs. In addition, the content of HCNTs in PHHCNT is higher than the feed contents of HCNTs in the reactants. The degradation temperature of PHHCNT increases and the weight loss decreases as the feed contents of HCNTs increase.

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