Polymer 50 (2009) 3652–3660

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Colloidal poly(styrene-co-butyl acrylate)/multi-walled carbon nanotubes nanocomposite by heterocoagulation in aqueous media

Sanghyun Hong [a], Jinho Hong [a], Dongsoo Jung [b], Sang Eun Shim [a,*]

[a] Department of Chemical Engineering, Inha University, 253 Yonghyundong, Namgu, Incheon 402-751, South Korea
[b] Department of Mechanical Engineering, Inha University, 253 Yonghyundong, Namgu, Incheon 402-751, South Korea

ARTICLE INFO

Article history:
Received 20 December 2008
Received in revised form
25 April 2009
Accepted 13 May 2009
Available online 9 June 2009

Keywords:
Nanocomposites
Colloids
Heterocoagulation

ABSTRACT

Colloidal nanocomposite particles were prepared by heterocoagulation of carbon nanotubes (CNTs) dispersion stabilized by cationic hexadecyltrimethylammonium bromide (CTAB) and negatively charged poly(styrene-co-butyl acrylate), P(St-co-BA), latex prepared by conventional emulsion polymerization in aqueous medium with the aid of a flocculant, polyaluminium chloride (PAC), at elevated temperature above the T_g of P(St-co-BA). The hybrid nanocomposite particles were prepared by a simple procedure consisting of mixing two dispersions, particle growth, and stabilization steps. The effects of the surface properties of CNTs, molecular weight of latex polymer, types of flocculants and its optimum concentration were investigated. At a well-controlled condition, the spherical or potato-like particles in the size range of 10–100 μm were achieved. After film formation of the nanocomposite particles, it was able to confirm that CNTs were uniformly distributed without agglomeration in the matrix, resulting in the percolation at a low concentration of CNTs.

1. Introduction

Due to the superior physical and chemical properties, carbon nanotubes (CNTs) have gained significant popularity in materials science since the discovery [1–3]. Young's modulus is over 1 TPa and the tensile strength is about 200 GPa. Additionally, they show metallic or semimetallic electric property according to the band structure [4–6]. These outstanding properties can be best exploited by incorporating CNTs into some forms of matrix. Therefore the preparation of CNT-containing composite materials is now a rapidly growing research area. In polymer society, CNTs are considered as an ideal filler to open new area by which various novel properties of composites can be achieved [7,8].

In order to use CNTs as a filler in polymers, it is crucial to make CNTs uniformly dispersed in host matrix. Either chemical or physical treatment of CNTs has been practiced to minimize self-agglomeration of CNTs, thereby to improve uniformity of dispersion. In chemical treatments, CNTs are covalently functionalized to have hydroxyl or carboxyl group. Although the functional groups are permanently preserved, the significant damages to the molecular framework of CNTs including sidewall opening, breaking, and transformation to amorphous carbon are resulted [9]. In turn, the deterioration of the properties of CNTs is experienced. Furthermore, environmental pollution is an inevitable problem. On the other hand, physical treatments of CNTs can overcome such problems in which CNTs are encapsulated by surfactants or dispersants. Although the choice of solvent is limited, the physical method has significant merits since the process is quite simple and the structure and properties of CNTs are unchanged [10].

CNT/polymer nanocomposites have been prepared by several conventional routes; melt compounding [11], *in-situ* polymerization [12], and solution processing [13]. Recently, polymer-based colloidal composite materials have brought much attention due to their unique three-dimensional structure and hybrid composition [14,15]. Generally, such composite particles have been prepared by incorporating guest materials into the heterogenous polymerization processes. A wide variety of inorganic materials have been used for the polymer-based hybrid colloidal particles, including titanium dioxide, copper oxide, magnetic oxide, aluminum hydroxide, alumina, clay, and so on. However, if the guest material is a radical scavenger or the agglomeration caused by strong van der Waals force is severe, desired composites cannot be prepared by *in-situ* polymerization, resulting in low conversion of monomer and poor dispersion in the matrix, respectively. Truly, CNTs have a remarkable radical trapping capability [16,17] and simultaneously tend to easily agglomerate due to a high aspect ratio.

Currently, the aggregation of colloidal particles has emerged as an interesting research topic in academic point of view. When the

---

[*] Corresponding author. Tel.: +82 32 860 7475; fax: +82 32 872 0959.
E-mail address: seshim@inha.ac.kr (S.E. Shim).

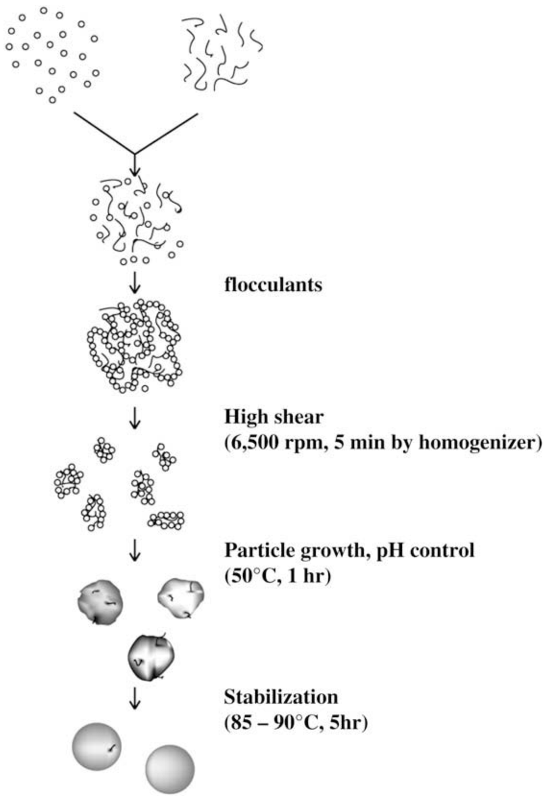
0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.05.060

Table 1
Properties of latex prepared by emulsion polymerization using various amounts of mercaptan.

Water (g)	Styrene (g)	BA (g)	SDS (g)	Mercaptan (g)	Molecular weight			T_g (°C)
					M_n (g/mol)	M_w (g/mol)	PDI	
200	12.3	7.7	0.454	–	102,870	319,370	3.11	40.2
				0.2	78,370	139,600	1.78	35.8
				0.4	17,480	84,950	4.86	31.9
				0.6	7010	43,180	6.16	27.6
				0.8	3520	24,800	7.05	25.0

equal particles in size and surface chemistry are involved, it is called homoaggregation [18], whereas heterocoagulation (or hetero-aggregation) is referred for the process with unequal particles [19]. This technology is now being extended to the fabrication of nano-structured materials. Mostly, various nanocomposites consisting of rubber latex and clay or layered silicate have been manufactured by this method [20–24]. In very recent years, the preparation of CNT-containing nanocomposites by a latex method has been introduced [25–30]. One of the advantages of this approach is that the percolation is achieved at a relatively low concentration of CNTs. However, some degree of the CNTs might not be incorporated into the latex matrix during the film formation process, resulting in the loss of CNTs. Therefore, we attempted to devise an improved method to minimize the loss of the CNTs.

In this publication, we explored the possibility to prepare CNT-containing colloidal nanocomposite where well-dispersed CNT dispersion having a positive charge was mixed with negatively charged poly(styrene-co-butyl acrylate), P(St-co-BA), emulsion latex prepared by emulsion polymerization. Two aqueous dispersions were mixed and an electrolyte was added to grow the composite particles. After the growing step, the shape of the hybrid materials was tuned to be spherical through a stabilization step. Finally, well-dispersed CNT-containing P(St-co-BA) colloidal particles were prepared without damaging the properties of CNTs. This latex heterocoagulation process can be extended to prepare CNT-containing nanocomposites of most vinyl polymers produced by heterogeneous polymerizations in a very simple route.



Scheme 1. Heterocoagulation process for synthesizing CNT-containing P(St-co-BA) colloidal nanocomposite in aqueous medium.

2. Experimental

2.1. Materials

The multi-walled CNTs synthesized by a thermal chemical vapor deposition (CVD) method were used (95% pure, Iljin Nanotech, Korea). The CNTs have a diameter of 10–20 nm and length of 10–50 μm. Styrene (Junsei, Samchun Chemical, Korea), butyl acrylate (Samchun Chemical), potassium persulfate (KPS, Aldrich), poly-aluminium chloride (PAC, 17% aqueous solution, E-Young Chemical, Korea), sodium chloride (NaCl, Acros Organics), magnesium chloride ($MgCl_2$, Acros Organics), hexadecyltrimethylammonium bromide (CTAB, Acros organics, 99+%) were purchased. Styrene and butyl acrylate were purified by a basic inhibitor removal column

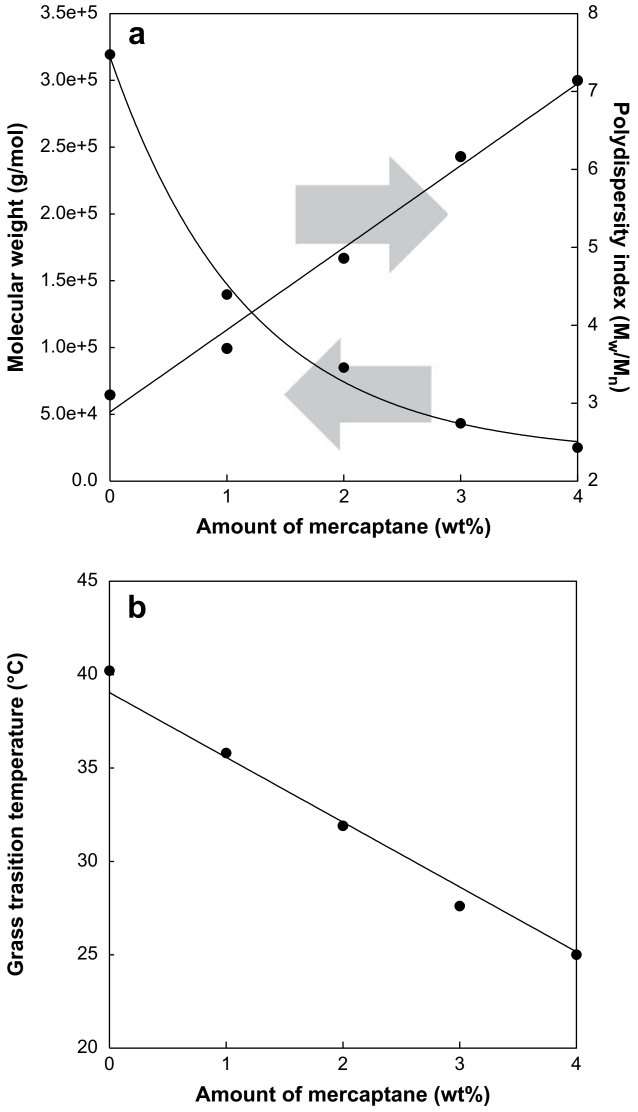


Fig. 1. Properties of latex prepared by emulsion polymerization with respect to the amount of mercaptan (a) molecular weight (M_w) and its distribution (PDI) and (b) the glass transition temperature (T_g).

(Aldrich) and stored at −5 °C prior to use. Mercaptan (1-dodecanethiol, 98.5+%, Acros Organics) and sodium dodecyl sulfate (SDS, 85%, Acros Organics) were used as received.

2.2. Preparation of CNT dispersions

Three types of 0.4 wt% CNT dispersions with the same CNT loading were prepared; carboxylated CNTs (CNT–COOH)/water, hydroxylated CNTs (CNT–OH)/water, and CTAB-stabilized CNTs/water. Carboxyl [31] and hydroxyl groups [32] were introduced on CNTs by following the well-established oxidation procedures. For the CTAB-stabilized CNTs/water, a predetermined amount of CTAB at c.m.c. was added to water. Note that the c.m.c of CTAB in water is 9×10^{-4} M at 25 °C. Zeta potentials of CNT–COOH/water, CNT–OH/water, and CTAB-stabilized CNTs/water were −25.3, −20.6, and +58.9 mV at pH 7.0, respectively.

2.3. Synthesis of latex by emulsion polymerization

P(St-co-BA) latex was synthesized by conventional emulsion polymerization. 200 ml water, 0.454 g SDS (at c.m.c), 12.3 g St, 7.7 g BA, and mercaptan were charged into 500 ml flask and emulsified using ultrasonication (Sonic & Materials Co., USA) for 3 min. The amount of the mercaptan as the chain transfer agent was varied from 0 to 0.8 g. When the temperature reached 70 °C, 0.2 g KPS dissolved in 10 ml water was poured into the flask and the polymerization was conducted under nitrogen atmosphere for 24 h. The resulting latex was analyzed in terms of molecular weight, glass transition temperature, and average size of the particles. After polymerization, solid content of the latex was about 9.8 wt%. Conversion measured by gravimetry was always over 98%. Zeta potential of the latex was −45.1 mV. The properties of the latex are summarized in Table 1.

2.4. Preparation of aqueous flocculant solutions

Three different types of the aqueous flocculant solutions were prepared; (1) 6 g of 17 wt% PAC solution mixed in 100 g water, (2) 35 g $MgCl_2 \cdot 6H_2O$ in 100 g water, and (3) 26 g NaCl in 100 g water.

2.5. Heterocoagulation process

The latex aggregation process is now explained by taking PAC solution as an example. All the procedures are the same for other flocculant solutions. 100 g P(St-co-BA) latex, 20 g CNT dispersion, and 2.0 g PAC solution were mixed by a homogenizer at 6100 rpm for 5 min at room temperature. The particle size grew up as the temperature of mixture increased to 50 °C for 1 h. In this step, CNTs were uniformly incorporated in polymer matrix by heterocoagulation. It is noted that pH was controlled to be 9.0 during the particle growth step. In order to control the ultimate morphology, temperature was further raised to 85–90 °C at which the nanocomposite formed a round i.e., spherical or potato-like i.e., simply meaning oblique spheroid possibly with bumps on the surface, shape by holding the temperature for 5 h. After repeated washing the colloidal nanocomposites with NaOH solution with pH 10.0 and water, the nanocomposite particles having the diameter in several tens of micrometers were prepared. The heterocoagulation process for making CNT-containing P(St-co-BA) nanocomposite particles is illustrated in Scheme 1.

2.6. Characterization

Turbiscan® (Formulation, France) was employed to investigate dispersion stability of CNT dispersions. The sedimentation behavior of the CNTs in water was monitored by measuring the backscattering and transmission of monochromatic light (λ = 880 nm) from the suspension. Suspensions in flat-bottomed cylindrical glass tubes (70 mm height, 27.5 mm external diameter) were placed in the instrument and the transmission of light from suspensions was then periodically measured along the height at room temperature. The results from transmission are presented as the sedimentation

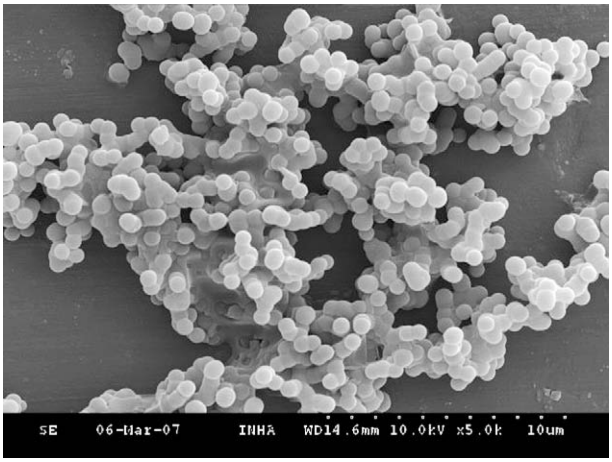


Fig. 2. SEM micrograph of P(St-co-BA) seed particles prepared by emulsion polymerization in the presence of 3 wt% mercaptan.

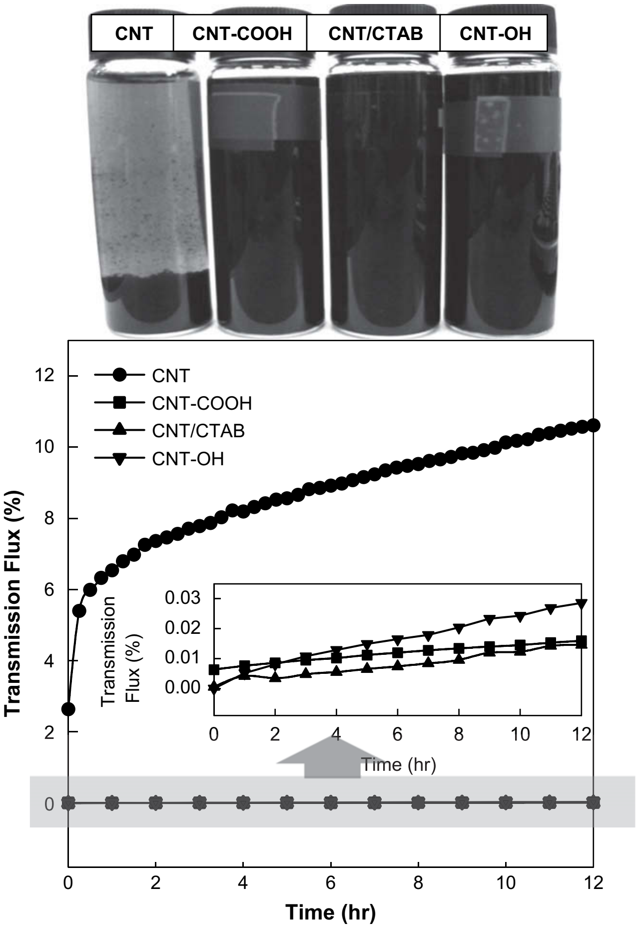


Fig. 3. Dispersion stability of various CNT dispersions in water; digital photographs (top) and the change transmission flux analyzed by Turbiscan® (bottom).

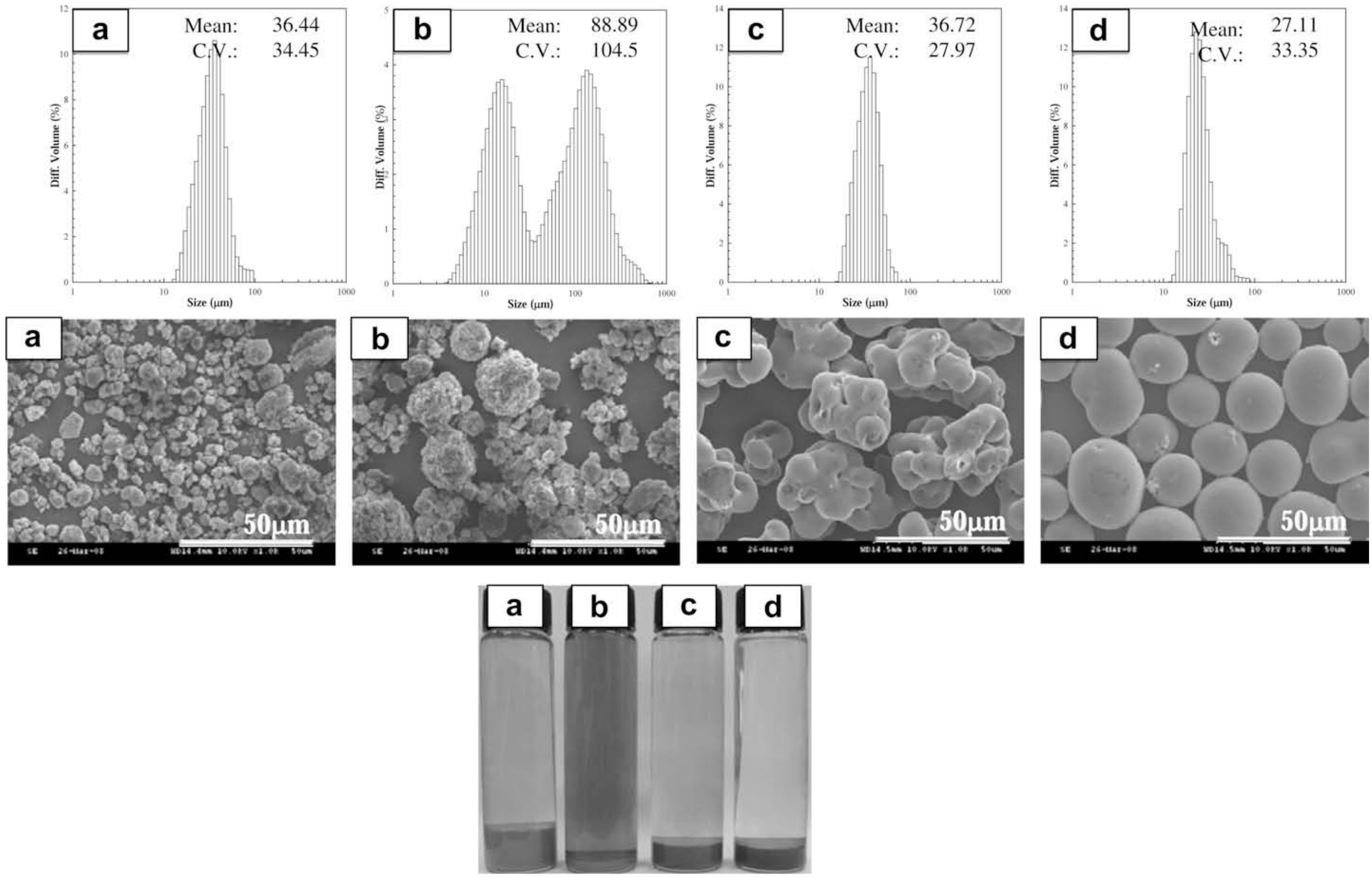


Fig. 4. Particle size distribution (top), the SEM morphology of the composite particles (middle), and final resultant in vials (bottom) using different seed particles polymerized with various amounts of mercaptan; (a) 0, (b) 1, (c) 2, and (d) 3 wt% (C2).

profile i.e., Δ transmission flux versus time. The size and size distribution of latex and nanocomposites were measured by a particle size analyzer (Coulter LS-230®, Beckman Coulter, USA). The scanning electron microscope (S-4300, Japan) and transmission electron microscope (CM200, Philips) were used to observe the morphology of the latex and nanocomposite particles. The molecular weight and the glass transition temperature of latex were measured with gel permeation chromatography (Viscotek VE series, USA) and differential scanning calorimeter (DSC200F3, Netzsch, Germany), respectively. The electrical conductivity of the composites was measured by resistivity meters (Hiresta-UP and Loresta-GP, Mitsubishi Chemical Co., Japan).

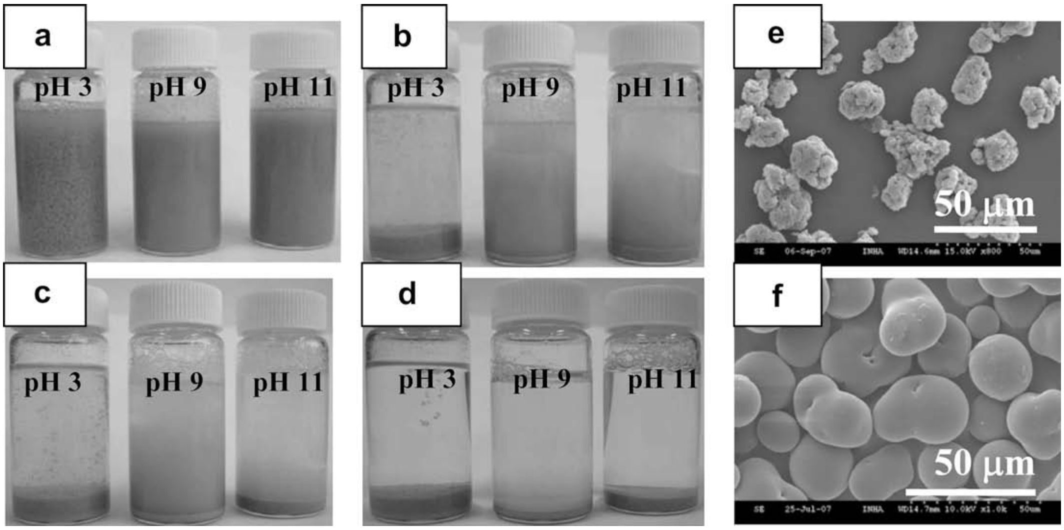


Fig. 5. Effect of pH on a stabilization step; (a) 0, (b) 15, (c) 30, and (d) 60 min. SEM micrographs of the hybrid particles (P2) after (e) the growth step and (f) stabilization step where pH 9.0 was used in the stabilization step. Refer to P1–P3 in Table 2. The seed particles were prepared with 3.0 wt% mercaptan and the ultimate composite particles contain 0.1 wt% CNTs.

Table 2
Experimental conditions for heterocoagulation between P(St-co-BA) latex and CNT dispersion using PAC as the flocculant and summarized results.

Sample	CNT content (wt%)	PAC solution (g/100 g latex)	pH control	Aggregated particle size (μm)
Blank	–	1.0	5.1 → 9.0	62.1
P1	CNT/CTAB 0.1	1.0	5.1 → 3.0	Mass
P2	CNT/CTAB 0.1	1.0	5.1 → 9.0	61.9
P3	CNT/CTAB 0.1	1.0	5.1 → 11.0	Mass
SC1	CNT/CTAB (0.0032) 0.1	1.0	5.1 → 9.0	48.9
SC2	CNT/CTAB (0.0130) 0.1	1.0	5.1 → 9.0	Mass
C1	CNT–COOH 0.1	1.0	5.1 → 9.0	35.9
C2 (P2)[a]	CNT/CTAB 0.1	1.0	5.1 → 9.0	61.9
C3	CNT–OH 0.1	1.0	5.1 → 9.0	39.0
F1	CNT/CTAB 0.1	0.6	5.1 → 9.0	Mass or no aggregation
F2	CNT/CTAB 0.1	0.8	5.1 → 9.0	Mass
F3	CNT/CTAB 0.1	1.2	5.1 → 9.0	Mass
CA1	CNT/CTAB 0.5	1.0	5.1 → 9.0	93.6
CA2	CNT/CTAB 1.0	1.0	5.1 → 9.0	67.7
CA3	CNT/CTAB 2.0	1.0	5.1 → 9.0	Mass
CA4	CNT/CTAB 5.0	1.0	5.1 → 9.0	Mass

[a] P2 = C2: control.

3. Results and discussion

3.1. Properties of P(St-co-BA) latex

The properties of the latex, especially, the molecular weight and corresponding glass transition temperature, might influence the entire heterocoagulation process since the chain mobility of the polymer is different. It is expected that the heterocoagulation process with CNTs will be successful for the polymer chains with the low molecular weight and glass transition temperature. Therefore, the lattices having different molecular weights and glass transition temperatures were prepared by varying the amount of mercaptan. When the chain transfer agent is present in radical polymerization, the radicals in growing polymer chains are transferred to the agent, resulting in the reduction in the molecular weight and increase in the polydispersity index. As seen in Fig. 1, the weight-average molecular weight (M_w) steadily decreases from 319,370 to 24,800 g/mol and the polydispersity index increases from 3.11 to 7.05 as the amount of mercaptan increases from 1.0 to 4.0 wt%. The glass transition temperature linearly decreases from 40.2 °C to 25.0 °C with the amount of mercaptan. The copolymers always had a single T_g. It is noted that the calculated glass transition temperature by Fox equation at this composition of St and BA without mercaptan is 31.68 °C. As the representative example, Fig. 2 shows the morphology of the latex prepared with 3 wt% mercaptan relative to monomer, where the number-average diameter of the seed particles is 90 nm with the coefficient of variation of 20.2%. The size of the seed particles is rarely changed by the amount of mercaptan. The zeta potential of the as-prepared seed latex is measured to be −45 mV at pH 3.0.

3.2. Dispersion stability of CNT dispersions

As seen in Fig. 3, fast sedimentation of pristine CNTs is observed, whereas the surface-treated CNTs have much improved dispersion stability in water even after 2 months. The stability of CNT dispersions is qualitatively analyzed by employing Turbiscan apparatus. Using Turbiscan, dispersion destabilization phenomena including particle size variation kinetics such as coalescence or flocculation and particle migration kinetics such as creaming or sedimentation are readily investigated even in concentrated or opaque emulsions or suspensions [33,34]. Inside Turbiscan cell, the backscattering (BS) and transmittance (T) of incident light are measured by calculating transport mean free path of photons (l^*) throughout the medium. Based on Mie theory, the BS and T can be obtained for a concentrated suspension as follows [35];

$$\mathrm{BS} \approx \left(1/l^*\right)^{1/2} \tag{1}$$

$$T \approx \exp(-r/l) \tag{2}$$

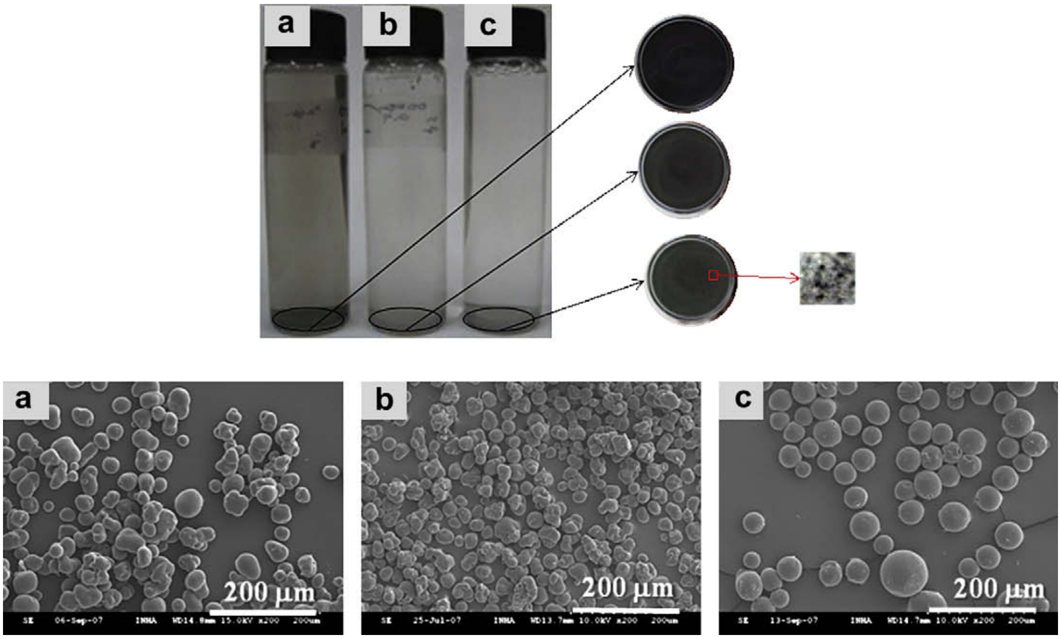


Fig. 6. The effect of the surface nature of CNTs on the heterocoagulation process; (a) carboxylated CNTs (C1), (b) CTAB-stabilized CNTs (C2), and (c) hydroxylated CNTs (C3). Sedimentation results (top) showing agglomerated CNTs for C1 and C3 and SEM micrographs (bottom) of hybrid particles containing 0.1 wt% CNTs after completion of the heterocoagulation process.

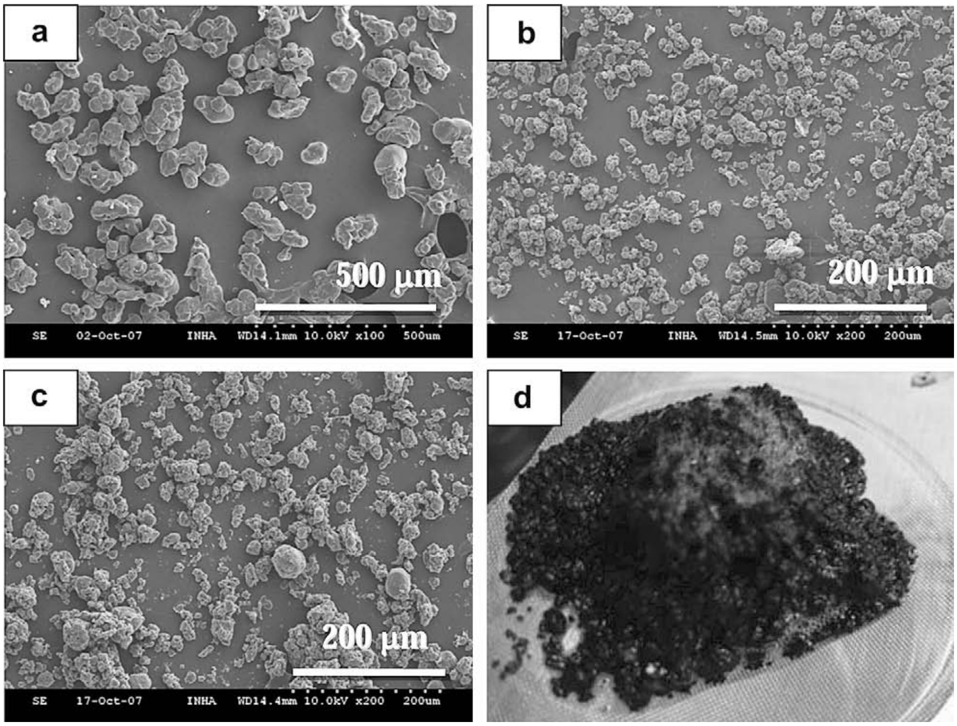


Fig. 7. SEM morphology of the final hybrid particles prepared with varying amounts of CNTs; (a) 0.5 (CA1), (b) 1.0 (CA2), (c) 2.0 (CA3), and (d) 5 wt% (CA4).

where r is an internal radius of a measurement cell. The photon transport mean free path (l^*) and photon mean free path (l) are defined;

$$l^* = \frac{2d}{3\Phi(1-g)Q_S} \tag{3}$$

$$l = \frac{2d}{2\Phi Q_S} \tag{4}$$

where d, Φ, g, and Q_S denote a particle mean diameter, the volume fraction of a dispersed phase, asymmetry factor, and scattering efficiency factor, respectively. The obtained results are presented as the sedimentation profile i.e., Δ transmission versus time.

CNTs tend to cohere in aqueous solutions due to their high surface energy and lack of chemical affinity with the dispersing medium. Pristine CNTs dispersed in water severely aggregate within 1 h and sedimentation continuously proceeds with time, resulting in the monotonous increase in transmission flux. On the other hand, the modified CNTs by carboxylic acid and carboxylic groups and CTAB-stabilized CNTs show much improved stability in water due to the chemical affinity between the polar modified groups and water. In the latter case, transmission flux hardly changes with time, less than 0.03% decrease for 12 h (inset to Fig. 3) since CNTs are colloidally stable in water. Strictly speaking, CNTs with carboxylic acid and CTAB-stabilized CNTs have better dispersion stability than CNTs with hydroxyl group. The zeta potential is an important indicative of ionically stabilized colloid systems. For modified CNT dispersions, the zeta potential values are high enough to provide the colloidal stability against coagulation; −25.3, −20.6, and +58.9 mV for CNT–COOH/water, CNT–OH/water, and CTAB-stabilized CNTs, respectively.

Table 3
Experimental conditions for heterocoagulation between P(St-co-BA) latex and CNT dispersion using $NaCl$ and $MgCl_2$ as the flocculant and summarized results.

Sample	Flocculant		Size and uniformity[a]	
	Type	Amount (g/100 g latex)	Average size (mm)	C.V.[a] (%)
N1	NaCl solution	14.0	Mass and no aggregation	
N2	NaCl solution	20.0	8.5	26.3
N3	NaCl solution	30.0	Mass	
M1	$MgCl_2$ solution	1.5	Mass and no aggregation	
M2	$MgCl_2$ solution	3.0	19.8	56.4
M3	$MgCl_2$ solution	4.5	Mass	

[a] Uniformity = the coefficient of variation (C.V.).

3.3. *Effect of the molecular weight of the latex*

Herein, the effect of the molecular weight and corresponding glass transition temperature on the heterocoagulation is investigated by using the seed particles prepared by various amounts of the mercaptan as shown in Fig. 4. Upon successful completion of the heterocoagulation followed by a stabilization process using 1 g PAC solution/100 g latex as the flocculant, the morphology of the ultimate particles containing 0.1 wt% CNTs (relative to polymer) stabilized by CTAB is expected to have a round and smooth surface. At high molecular weight (M_w) above 100,000 g/mol, the ultimate particles have a poorly controlled shape; the size distribution is broad or bimodal and the surface is coarse (Fig. 4a and b). As the molecular weight further decreases below 100,000 g/mol, the surface changes to be smooth and finally spherical; intermediate morphology with M_w of 84,950 g/mol and a well-controlled shape with M_w of 43,180 g/mol with average diameter of 27.1 µm and narrow size distribution of 33.35%. It is noted that the resulted medium after heterocoagulation is still dark for the seed particles with a high molecular weight above 100,000 g/mol, whereas the medium is transparent for the molecular weight of 43,180 g/mol (Fig. 4d). The high degree of transparence of the medium upon the completion of the entire process indicates that all CNTs are embedded into the matrix phase. Based on the results, one can conclude that the low molecular weight of the latex is preferred for the heterocoagulation process since the mobility of the polymeric chain is greater. Therefore, the seed particles having M_w of 43,180 g/mol prepared with 3 wt% mercaptan were chosen for the following sets.

3.4. Significance of pH control during particle growth

The pH during the particle growth step in which heterocoagulation occurs is an important parameter since pH determines interactions between the two different colloidal species. The heterocoagulation process was monitored by taking aliquot of samples from the reactor in the growth step. Before the growth step, the mixture of latex and CNTs dispersion has pH 5.1. Fig. 5 represents the effect of pH on the heterocoagulation process. At low (pH 3.0) and high (pH 11.0) pH, the latex and CNT dispersion severely heterocoagulated, resulting in the very fast sedimentation at early stage, 15 min. In this case, the colloidal nanocomposite is not obtainable. However, heterocoagulation undergoes in a controlled manner at pH 9.0 since the electrostatic attraction is favored. The SEM micrographs of the resultant hybrid particles show that the latex and CNTs grow up in individually stable particles during/after the growth step (Fig. 5e), and they finally give a controlled potato-like or spherical shape upon finishing the stabilization process (Fig. 5f). At pH 9.0, the ultimate particles have number-average diameter of 61.9 μm (P2 in Table 2). In the absence of CNTs, the P(St-co-BA) seed latex undergoes homoaggregation to give 62.1 μm sized particles.

3.5. Effects of surface nature of CNTs, amount of flocculant, and loading of CNTs

By adopting conditions found in the previous sections, the heterocoagulation process was investigated by varying the surface nature of CNTs and the amount of the flocculant, PAC solution. In Fig. 6, three different types of CNTs are employed for the heterocoagulation process; CNT–COOH, CTAB-stabilized CNT, and CNT–OH. It seems that well-controlled (individually stable) hybrid particles can be prepared regardless of the surface nature of CNTs according to SEM micrographs. However, one can see that a significant portion of CNTs is self-agglomerated and settled down for carboxylated and hydroxylated CNTs by simply interacting with PAC molecules. The black spots at the bottom of the vial are the agglomerated CNTs as representatively shown in Fig. 6c. However, all CTAB-stabilized CNTs are well incorporated within the matrix particles during the particle growth step, thereby the serum is most transparent and no black spot is observed (Fig. 6b). This result originates from the electrostatic attraction between the positive CNT dispersion and negatively charged latex.

The effect of ionic strength on the heterocoagulation process is also investigated by varying amount of PAC solution, 0.6–1.2 g (refer to Supporting information). With 0.6 and 0.8 g PAC solution, some latex particles are heterocoagulated and settled down; however, large portion of the latex still exists in the medium, resulting in turbidity after the heterocoagulation. Also, severe and instant coagulation is observed upon the addition of the 1.2 g PAC solution. Therefore, the optimum amount of PAC solution lies between the two limits, which are near 1.0 g as shown in Figs. 4d, 5f, and 6b.

Now, as shown in Fig. 7, the amount of CNTs is further increased from 0.1 wt% to find the maximum loading. As the amount of CNTs increases to 2.0 wt% relative to the amount of latex solid content, we still obtain individually existing CNT-containing nanocomposite particles. With increased amount of CNTs, the surface of the hybrid particles is not round any longer after stabilization process since it

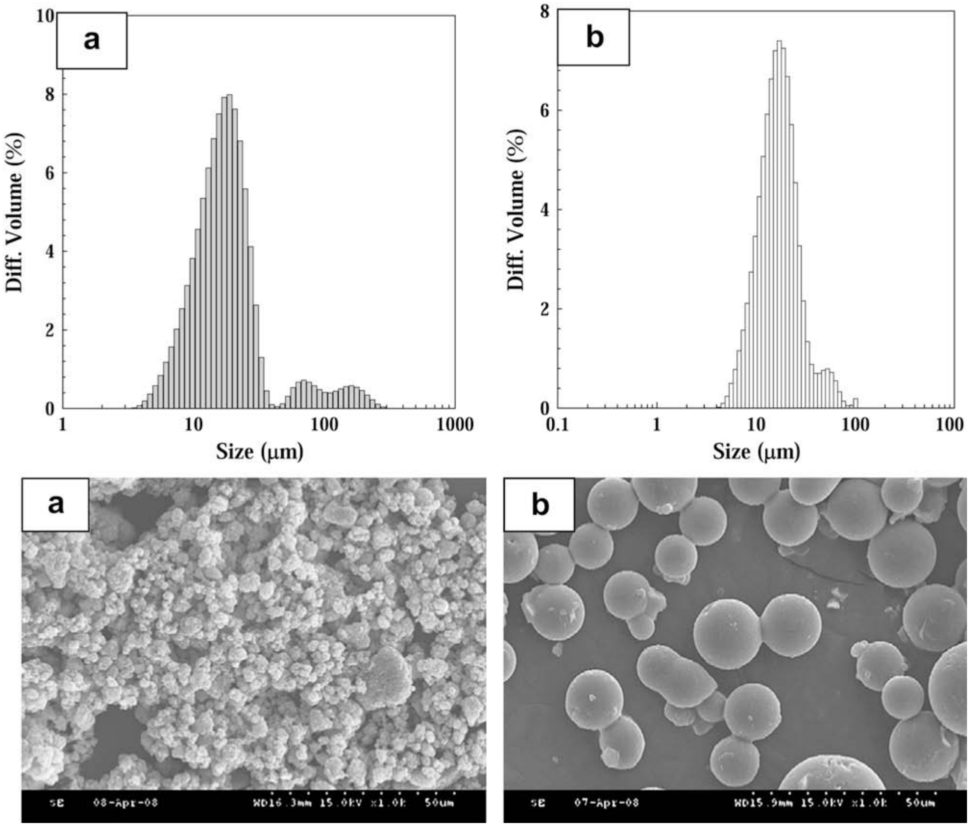


Fig. 8. Size distribution (top) and morphology (bottom) of the hybrid particles containing 0.1 wt% CNTs prepared with (a) NaCl (N2) and (b) $MgCl_2$ (M2) as the flocculant.

is now thermally resistant due to the high loading of CNTs. At 5 wt% CNT loading, the particle growth process was successful; however, we could not obtain controlled morphology after the stabilization process (Fig. 7d). The experimental conditions and the results hitherto are given in Table 2.

3.6. *Effect of the type of flocculants*

Herein, we investigated the feasibility of replacement of flocculants instead of PAC, where weaker electrolytes, NaCl and $MgCl_2$, were employed. The optimum conditions are found by repeated experiments and the brief results are summarized in Table 3. With 20.0 g NaCl and 3.0 g $MgCl_2$ solutions, we were also able to prepare individually stable hybrid composite particles by the heterocoagulation process. It is natural that the necessary amount of the electrolyte is $NaCl \gg MgCl_2 > PAC$ in accordance with the inverse degree of the ionic strength of the electrolyte. Fig. 8 indicates that $MgCl_2$ results in a well-controlled final shape (Fig. 8b), whereas the heterocoagulation capability of NaCl is low so that great number of small particles is still present (Fig. 8a).

3.7. *Morphology of the ultimate hybrid nanocomposite*

The morphology of the hybrid nanocomposite particles and prepared film is represented in Fig. 9 in which the hybrid particles contain 0.1 wt% CNTs. The TEM image (Fig. 9a) of the cryogenically microtomed section of the CNT-containing hybrid particles shows that CNTs are embedded without agglomeration inside the matrix particles. The nanocomposite film containing CNTs was prepared on glass substrate heating the hybrid particles at 60 °C in vacuum oven. The film was cryogenically fractured and its cross-section was monitored by SEM (Fig. 9b). At high magnification, it is seen that CNTs are evenly distributed throughout the matrix without agglomeration, indicating that the CNTs in the hybrid particles produced by the heterocoagulation are successfully transferred to the film. This result implies that one can simply fabricate CNT-

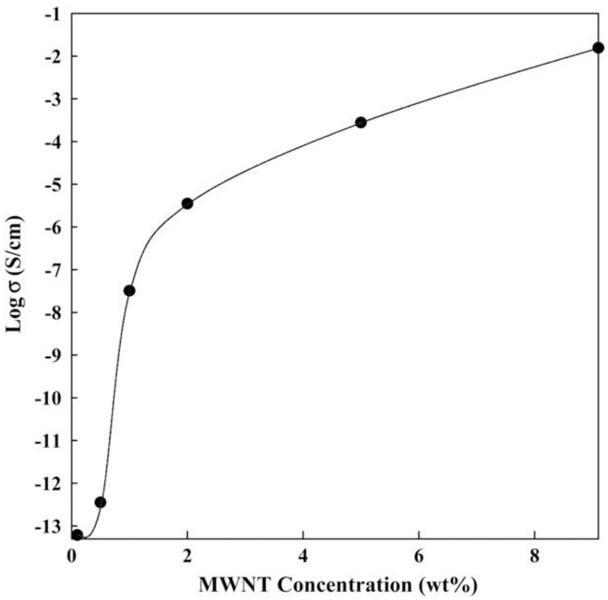


Fig. 10. The electrical conductivity of P(St-co-BA)/CNT nanocomposite prepared by heterocoagulation in aqueous media.

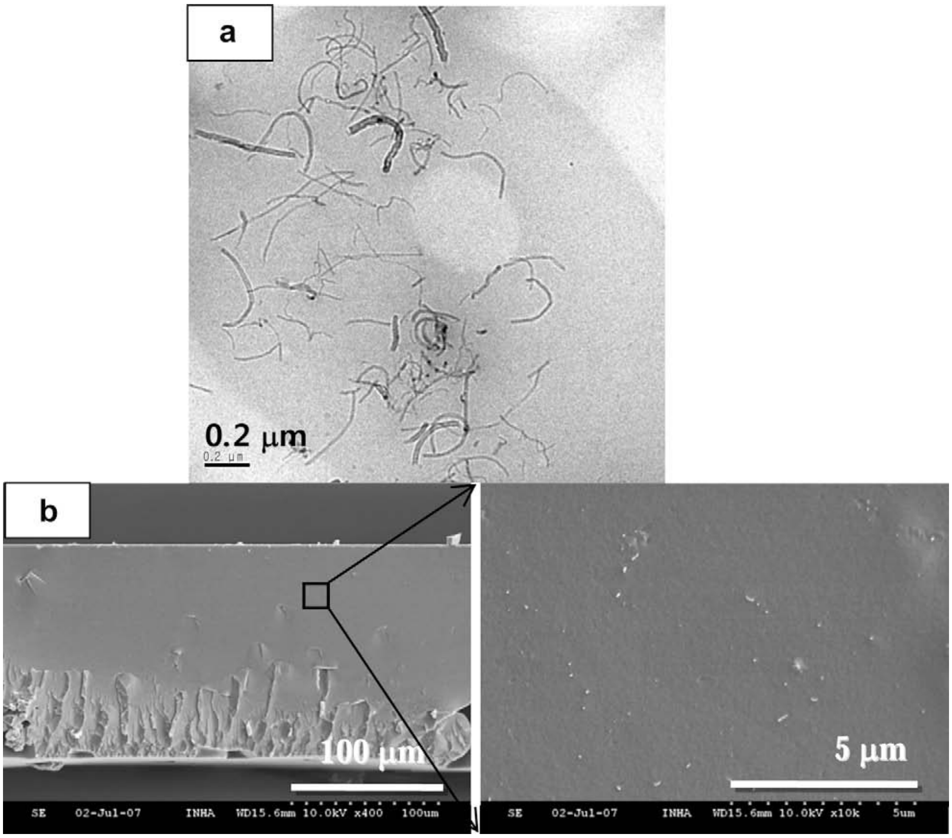


Fig. 9. (a) TEM morphology of cross-section of the hybrid particles containing 0.1 wt% CNTs (C2) and (b) SEM morphology of the fractured surface of the film prepared with sample C2.

containing nanocomposites by a heterocoagulation process in aqueous medium.

3.8. Electrical conductivity of the composites

The electrical conductivity of the composites is presented in Fig. 10. The value increases from 6.12×10^{-14} to 1.56×10^{-2} S/cm. The abrupt increase at 0.5–1.0 wt% CNTs due to percolation is found. In many reports, the conductive percolation threshold was found at 3–10 wt% as mentioned in Ref. [27]. Therefore, this heterocoagulation process can be considered as an effective tool to prepare nanocomposites with a high electrical conductivity at a low concentration of CNTs.

4. Conclusions

In this work, colloidal nanocomposite particles were prepared in aqueous medium by heterocoagulation of CNTs and P(St-co-BA) latex. The CNT dispersion stabilized by a cationic surfactant, CTAB, and negatively charged P(St-co-BA) latex prepared by conventional emulsion polymerization were mixed and flocculant was added to proceed heterocoagulation. In the particle growth step at 50 °C, the CNTs are uniformly embedded into the polymer matrix. Throughout the stabilization step at 85–90 °C, the hybrid particles are manipulated to have a round shape. It was found that the molecular weight of the seed latex below 100,000 g/mol was effective since the chain mobility is high enough. When CNTs were negatively treated by surface functionalization, CNTs were only partially incorporated into the matrix. Colloidally stable particles were achieved by modulating the pH to be 9.0 during the particle growth step. The amount of PAC solution as the flocculant also affected the heterocoagulation process. At a well-controlled condition, the spherical or potato-like particles in the size range of 10–100 μm were achieved. After film formation of the nanocomposite particles, it was able to confirm that CNTs were uniformly distributed without agglomeration in the matrix. This study suggests a route to prepare polymer/CNT nanocomposite materials by a simple process in the aqueous medium.

Acknowledgement

This work was supported by the Korea Science and Engineering Foundation (grant no. R01-2007-000-20055-0).

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.05.060.

References

[1] Ijima S. Nature 1991;354:56–8.
[2] Calvert P. Nature 1999;399:210–1.
[3] Shaffer MSP, Windle AH. Adv Mater 1999;11:937–41.
[4] Baughman RH, Cui CX, Zakhidov AA, Iqbal Z, Barisci JN, Spinks GM, et al. Science 1999;284:1340–4.
[5] Yu MF, Lourie O, Dyer MJ, Moloni K, Kelly TF, Ruoff RS. Science 2000;287:637–40.
[6] Strano MS, Dyke CA, Usrey ML, Barone PW, Allen MJ, Shan HW, et al. Science 2003;301:1519–22.
[7] Ajayan PM, Schadler LS, Giannaris C, Rubio A. Adv Mater 2000;12:750–3.
[8] Breuer O, Sundararaj U. Polym Compos 2004;25:630–45.
[9] Monthioux M, Smith BW, Burteaux B, Claye A, Fischer JE, Luzzi DE. Carbon 2001;39:1251–72.
[10] Strano MS. Nat Mater 2006;5:433–4.
[11] Grady BP, Pompeo F, Shambaugh RL, Resasco DE. J Phys Chem B 2002;106:5852–8.
[12] Allaoui A, Bai S, Cheng HM, Bai JB. Polym Compos Sci Technol 2002;62:1993–8.
[13] Salvetat JP, Bonard MJ, Thomson NH, Kulik AJ, Forro L, Benoit W, et al. Appl Phys A 1999;69:255–60.
[14] Caruso F. Adv Mater 2001;12:11–22.
[15] Sanchez C, Soler-Illia GJAA, Ribot F, Lalot T, Mayer CR, Cabuil V. Chem Mater 2001;13:3061–83.
[16] Kitano H, Tachimoto K, Gemmei-Lde M, Tsubaki N. Macromol Chem Phys 2006;207:812–9.
[17] Fenoglio I, Tomatis M, Lison D, Muller J, Fonseca A, Nagy JB, et al. Free Radic Biol Med 2006;40:1227–33.
[18] Behrens SH, Christl DI, Emmerzael R, Schurtenberger P, Borkovec M. Langmuir 2000;16:2566–75.
[19] Islam AM, Chowdhry BZ, Snowden MJ. Adv Colloid Interface Sci 1995;62:109–36.
[20] Hwang WG, Wei KH, Wu CM. Polymer 2004;45:5729–34.
[21] Wang YZ, Zhang LQ, Tang CH, Yu DS. J Appl Polym Sci 2000;78:1879–83.
[22] Wu YP, Wang YQ, Zhang HF, Wang YZ, Yu DS, Zhang LQ, et al. Compos Sci Technol 2005;65:1195–202.
[23] Varghese S, Karger-Kocsis J. Polymer 2003;44:4921–7.
[24] Varghese S, Gatos KG, Apostolov AA, Karger-Kocsis J. J Appl Polym Sci 2004;92:543–51.
[25] Dufresne A, Paillet M, Canet R, Carmona F, Delhaes P, Cui S. J Mater Sci 2002;37:3912–23.
[26] Grunlan JC, Mehrabi AR, Banoon MV, Bahr JL. Adv Mater 2004;16:150–3.
[27] Regev O, Elkati PNB, Loos J, Koning CE. Adv Mater 2004;16:248–51.
[28] Grossiord N, Loos J, Koning CE. J Mater Chem 2005;15:2349–52.
[29] Grunlan JC, Kim YS, Ziaee S, Wei X, Abdel-Magid B, Tao K. Macromol Mater Eng 2006;291:1035–43.
[30] Wang T, Lei CH, Liu D, Manea M, Asua JM, Creton C, et al. Adv Mater 2008;20:90–4.
[31] Chen J, Hamon MA, Hu H, Chen Y, Rao AM, Eklund PC, et al. Science 1998;282:95–8.
[32] Zhang N, Xie J, Varadan VK. Smart Mater Struct 2002;11:962–5.
[33] Buron H, Mengual O, Meunier G, Gayré I, Snabre P. Polym Int 2004;53:1205–9.
[34] Chanamai R, McClements DJ. J Colloid Interface Sci 2000;225:214–8.
[35] Snabre P, Mengual O, Meunier G. Colloid Surf A 1999;152:79–88.