Int. J. of GEOMATE, March, 2012, Vol. 2, No. 1 (Sl. No. 3), pp. 161-165
Geotec., Const. Mat. and Env., ISSN:2186-2982(P), 2186-2990(O), Japan

Development of Functional Carbon Nanotubes -Asphalt Composites

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ABSTRACT: The purpose of this study is to prepare asphalt composites containing CNTs and to elucidate the characteristic properties of CNTs-dispersed asphalt composites. In the present study, such composites were prepared using several types of asphalt emulsions as a binder. As a result, both nonionic and anionic emulsions kept dispersed state, when combined with as-prepared CNTs. However, cationic emulsions failed to keep dispersed state. After several additional systematic experiments, it was found that cationic emulsion successfully retained an adequate dispersion state, when as-prepared CNTs were treated with acid solution and the following incremental addition of the pretreated CNTs. The three types of CNTs-asphalt composites demonstrated higher performances in both penetration and microwave-absorption tests than asphalt composites including carbon black powder instead of CNTs, when the mass percentage of all carbon materials was the same.

Keywords: Carbon nanotubes -asphalt composites, Asphalt emulsion, Acid treatment, Absorption of microwave

1. INTRODUCTION

In recent years, nanocarbon materials such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been attracting much global attention as potential fillers for improving the mechanical and electrical characteristics of cement mortars in many countries [1]. However, there has not been much investigation into the application of nanocarbon materials for asphalt pavement [2].

CNTs are well known for their superior performances in mechanical, thermal, and electrical performance [3]. A CNT has a very high aspect ratio and so it probably acts as a bridge between grains of sand, suggesting that CNTs-enriched asphalt have the potential to reinforce asphalt pavement. Moreover, CNTs are highly electro-conductive and therefore CNT-enriched asphalt will surely absorb microwave and increase in temperature. Often, the resulting temperature is high enough to melt solid asphalt into liquid asphalt that can combine grains of sand and gravel. This novel form of asphalt manipulation may provide a new way to pave roads with asphalt.

CNTs are thought to be too expensive to use as construction materials. Recently, however, a new production process, which will possibly lower the cost of CNTs, has been reported [4]. The process, which was named direct methane reforming (DMR) process, can provide CNTs as a by-product of hydrogen production from natural gas using catalysts. In this process catalyst materials remain in as-prepared CNTs and so the purification is necessary to obtain CNTs of high purity. Especially, CNTs for the uses of a lithium ion battery, electronic devices, etc. should be of higher purity. CNTs have a variety of uses. For some uses, CNTs of not so high purity will serve their purpose. A paving material is one example. In this case CNTs are used as a filler of high mechanical strength due to their high aspect ratio.

The purpose of this study is to prepare new asphalt composites containing CNTs and to elucidate the characteristic properties of CNTs dispersed asphalt composites. Since asphalt is not fluid at ordinary temperatures, it does not act as a binder of aggregate. Therefore, asphalt is usually heated at elevated temperatures to lower the viscosity before its use. Another methods of fluidizing without heating are the addition of a solvent to asphalt and the emulsification of asphalt with water using surface-active agents. Asphalt emulsions, namely, colloidal dispersions of asphalt particles in water have low viscosity and so are easily mixed with aggregate even at ordinary temperatures. Asphalt emulsions were made by emulsifying high-viscosity asphalt into water with the aid of surface-active agents. The mixture of asphalt-emulsion and aggregate became very strong, because the aggregate became bound together with asphalt after water was removed off.

In order to disperse CNTs into a liquid, surface-active agents are frequently used. Although surface-active agents that are used in asphalt emulsions are not common to those of CNTs, the former agents could be act as the latter agents. If so, asphalt emulsions, which are inexpensive, are suitable materials for adding of CNTs. In this study, such composites were prepared using several types of asphalt emulsions instead of conventional asphalt which needs preheating.

2. EXPERIMENTAL

2.1 Figures and Tables

a) Asphalt emulsions as binders

As asphalt binders, cationic, anionic and nonionic asphalt emulsions were used (Table 1) [5]. All asphalt emulsions were provided by Nichireki Corporation. It is noteworthy that the pH of every asphalt emulsion is different; cationic emulsion is acidic, nonionic emulsion is neutral and anionic emulsion is alkaline.

b) Carbon fillers

CNTs and carbon black are used as carbon fillers (Table 2) [6]. The CNTs were produce by the direct methane reforming reaction using an iron catalyst [4].

An industrial carbon black sample was provided by Tokai Carbon Corporation. Its arithmetical mean particle size (the primary particles) was 28nm [7]. Another carbon black sample also was produced by the direct methane reforming reaction using another iron catalyst. The

Table 1 Characteristics of asphalt emulsions

Emulsion type		Viscosity (B type) 25°C (cP)	pH	Reduction of mass during evaporation (wt%)
Cationic	For permeation	50.2	1.93	67.06
	Tuck coat	19.9	2.40	50.49
	For mixing MK-2（JIS K 2208）	178.9	4.66	57.70
Nonionic	For mixing MN-1（JIS K 2208）	35.5	6.90	56.60
Anionic		525.0	12.89	65.05

Table 2 Bulk density measurements of carbon fillers

No.	Carbon filler	Bulk density (g/cm^3)	Ratio to the density of sample A
A	As-prepared CNTs	0.0289	1.00
B	As-prepared CNTs after milling	0.1048	3.63
C	Acid treated CNTs (HCl)	0.1503	5.20
D	Acid treated CNTs (HNO_3)	0.1517	5.25
E	Carbon black produced by the DMR method	0.1030	3.57
F	Industrial carbon black	0.3380	11.7

Table 3 Dispersibility of carbon fillers in asphalt emulsions

Emulsion type		pH	As-prepared CNTs		Acid treated CNTs (with HCl or HNO_3)		Industrial carbon black
			Addition at once	Incremental addition	Addition at once	Incremental addition	Addition at once
Cationic	For permeation	1.93	Poor	Poor (Agglomerate)	Poor	Fair	Fair
	Tuck coat	2.40	Poor	Fair	Fair	Good	Good
	For mixing MK-2（JIS K 2208）	4.66	Poor	Fair	Fair	Good	Good
Nonionic	For mixing MN-1（JIS K 2208）	6.90	Excellent	--	Excellent	--	Excellent
Anionic		12.89	Good	--	Good	--	Good

as-prepared CNTs were treated with dilute solution of hydrochloric acid (HCl) or nitric acid (HNO3) followed by filtering with suction.

2.2 Preparation of carbon filler-asphalt composites

CNTs or carbon black of 0.40g was added into an asphalt emulsion of 40g and then mixed using a magnetic stirrer. The resulting samples were dried in a dry oven maintained at 70°C until constant weight was reached.

2.3 Penetration test

The penetration test (JIS K 2208) was adopted as a standard test of hardness evaluation of asphalt materials.

2.4 Absorption of electric magnetic wave

The microwave-absorption ability of the filler-emulsion composites was evaluated by measuring a rise in the surface temperature. This is because microwave absorbed by a sample is converted into thermal energy to result in a temperature rise. Every sample was irradiated with microwave of 500W for 10 seconds. The temperature measurements were done with a radiation thermometer.

3. RESULTS AND DISCUSSIONS

3.1 Dispersion of carbon fillers into asphalt emulsions

Table 3 summarizes the dispersibility of the carbon fillers to different types of asphalt emulsions.

3.1.1 Effects of asphalt emulsions

a) Nonionic emulsion

The two types of carbon black samples became dispersed in the nonionic emulsion by stirring in a short time. And as-prepared CNTs also became dispersed in the nonionic emulsion by stirring in over 5min.

b) Anionic emulsion

In the case of anionic emulsion that has higher viscosity than nonionic emulsion, both CNTs and two types of carbon black samples also dispersed, although the necessary time for stirring was longer than in the case of nonionic emulsion.

c) Cationic emulsion

In the case of the cationic emulsions, however, the degree of dispersion depended on both the kind of a carbon-filler and the type of an asphalt emulsion.

The two types of carbon black samples were dispersed in

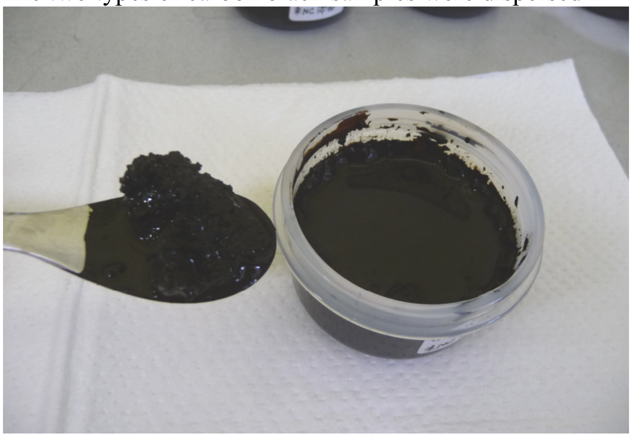

Fig. 1 Agglomeration on cationic emulsion surface

both MK-2 emulsion (JIS K 2208), which is frequently used for surface treating of wearing course and modified asphalt emulsion for tuck coat layer.

On the other hand, it was difficult to disperse the as-prepared CNTs were not dispersed instantly; CNTs particles stayed for a while in the upper zone of the MK-2 emulsion and modified-asphalt emulsion (Fig. 1).

This suggests that the wettability of the CNTs by the cationic asphalt emulsion is not good.

3.1.2 Effects of CNTs-addition methods

a) MK-2 emulsion

Although carbon black samples added at once was dispersed into MK-2 emulsion regardless of the quantity, CNTs failed to disperse when a large quantity of CNTs was added at one time. However, the same quantity of CNTs was managed to disperse when the CNTs were subdivided ... rementally ... art of CN ... tate is ach

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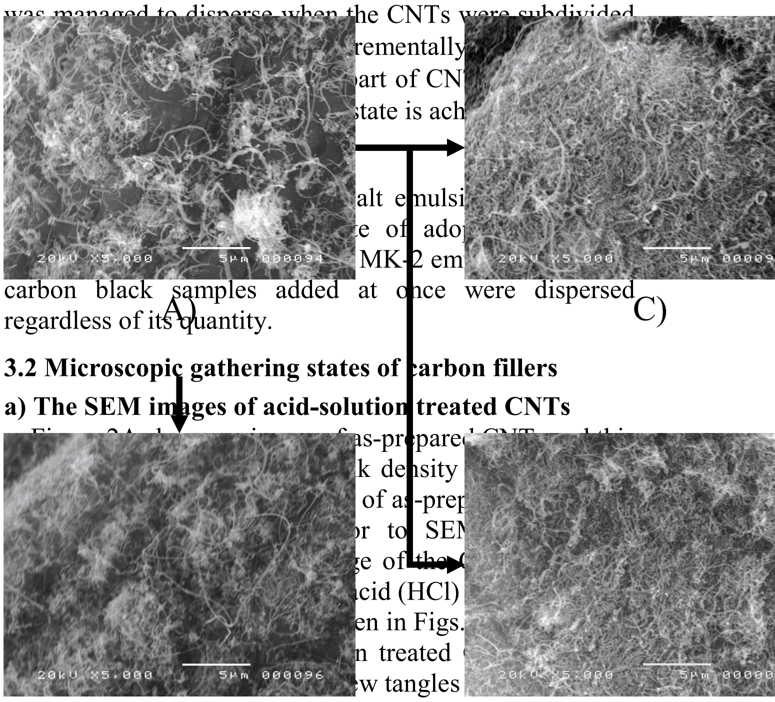

3.2 Microscopic gathering states of carbon fillers

a) The SEM images of acid-solution treated CNTs

... as-prepared ... k density ... of as-prep ... r to SEM ... e of ... cid (HCl) ... en in Figs. ... n treated ... w tangles

This situation seems to be a good condition to scatter the CNTs in asphalt emulsion, resulting in a good dispersion. Figures 2E and 2F show the images of homemade carbon black and industrial carbon black respectively. The shape of their samples is clearly different from that of CNTs (seen in Figs. 2A-2D). The former is spherical, while the latter is fibrous.

Fig. 2 Effects of milling or acid treatment on as-prepared CNTs (SEM: 5,000 times)

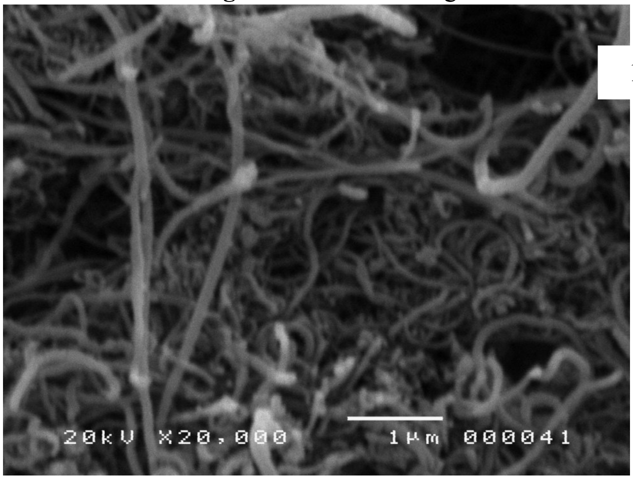

Fig. 3 SEM image of as-prepared CNTs (20,000 times)

3.3 CNTs and their acid-solution treatment

a) SEM images of carbon fillers

Figure 2 shows a scanning electron microscopy (SEM) image of as-prepared CNTs with a magnification of 20,000. A secondary electron is discharged from iron particles attached on tops of the CNTs and whitens with the SEM image. Each iron particle was a constituent of the iron catalysts used for producing the CNTs, clearly indicating that catalysts remain in the as-prepared CNTs (Fig. 3).

A result of the analysis with the energy dispersion type fluorescence X-ray analyzer (XRF-EDX) revealed that as-prepared CNTs included a catalyst (iron: 4.3wt%).

In Fig. 2, the CNTs (diameter: ~100nm) flex in the shape of a fiber and grow up while twisting and tangling. When the CNTs twist up, a cavity occurs in the CNTs. As a result, the bulk density of the CNTs is low.

b) Acid–solution treatment of CNTs

As a result, the bulk density of the CNTs shrinks. Therefore, it is thought that preprocessing to reduce the amount of remaining catalyst is important. An acid–solution treatment of the CNTs was carried out in anticipation of the improvement in degree of their dispersion. When the as-prepared CNTs contact the acid solution (Fig. 4), every iron particle in the residual catalyst (fine particles of iron) is dissolved into the solution.

Two specimens of the acid-solution treated CNTs samples were measured by the XRF-EDX method and it was found that the concentration of residual catalyst (iron) was 2.0wt% and 1.7wt% respectively. The concentrations are almost as in half as that of as-prepared CNTs, indicating that the acid-solution treatment is useful to improve the purity of the CNTs.

c) Bulk density

Table 2 lists the results of measuring the bulk density of the same samples shown in Fig. 2. The bulk density of as-prepared CNTs increased after milling or treating with the acid-solution. This change in density probably occurs because the bulky agglomerate of as-prepared CNTs was disentangled and compacted.

3.4 Degree of dispersion of acid-solution treated CNTs emulsions

a) Nonionic and anionic emulsions

The CNTs became dispersed in the nonionic emulsion after stirring in a short time, indicating the affinity of both

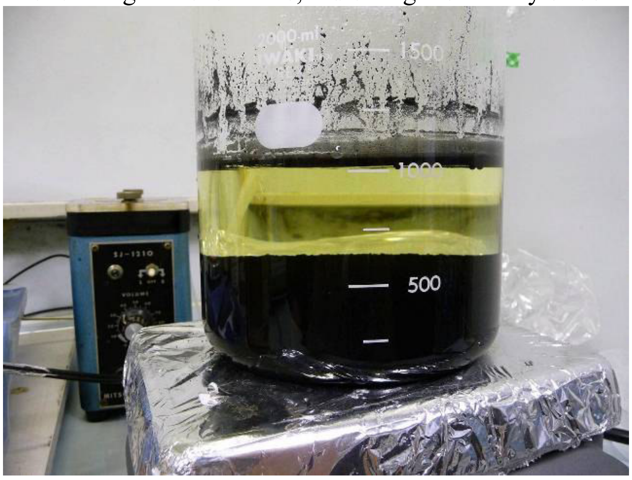

Fig. 4 Treatment of as-prepared CNTs with a dilute hydrochloric acid solution

filler with the liquid is very high. In the case of anionic emulsion that has higher viscosity than nonionic emulsion, both CNTs needed longer time than in nonionic emulsion to reach a similarly state of dispersion.

b) Cationic Emulsions

In the case of the emulsion of MK-2 or tuck coats, acid-solution treated CNTs fairly dispersed when a large quantity of the CNTs was added at one time. And the degree of dispersion became good when the CNTs were added incrementally.

In the case of modified-asphalt emulsion, acid-solution treated CNTs hardly dispersed when a large quantity of the CNTs was added at one time. However, the CNTs fairly dispersed when the CNTs were added incrementally.

3.5 Improved dispersibility of acid-solution treated CNTs into cationic emulsions

The acid solution dissolved iron particles in as-prepared CNTs, releasing ferric ions (Fig. 4). In the same manner, the cationic emulsions, which are strong acid, probably dissolves iron particles in as-prepared CNTs.

The ferric ions will interact with a surface-active agent that contributed to stabilize the cationic emulsions and take away its important role, resulting in the agglomeration. The reason as-prepared CNTs failed to disperse is that the ferric ions released from the residual catalyst in as-prepared CNTs.

This change in bulk density probably occurs because the bulky agglomerate of as-prepared CNTs was disentangled and compacted.

3.6 Characteristics of CNTs -asphalt composites

a) Penetration test

Figure 5 shows the results of penetration test (JIS K

2208) for CNTs-emulsion composites. Apparently a CNTs- emulsion composite was more greatly stiffened by adding CNTs than carbon black of the same mass concentration. In other words, CNTs can give the same penetration degree as carbon black samples with a lesser quantity of addition.

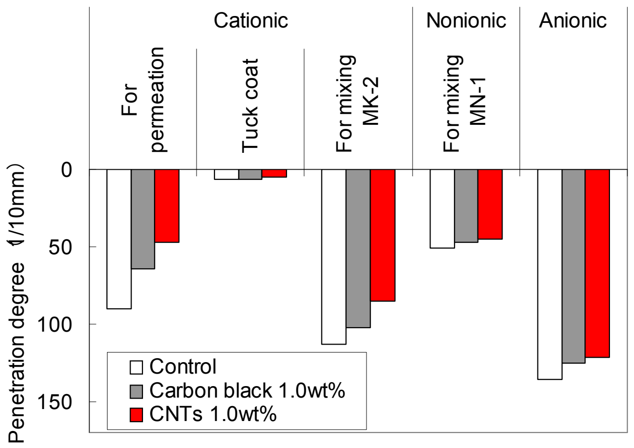

Fig. 5 Results of penetration tests

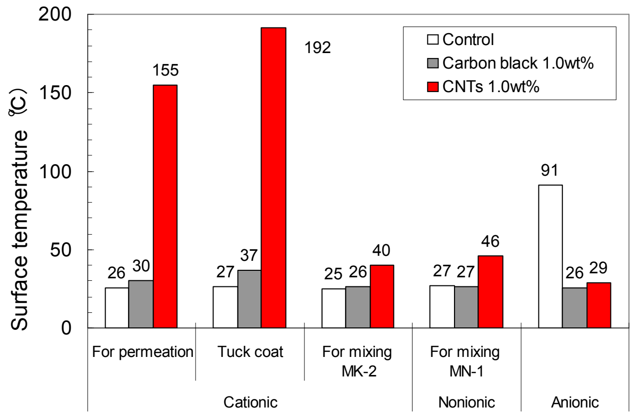

Fig. 6 Temperature change of carbon fillers by microwave irradiation

b) The absorption of microwave by CNTs-emulsion composites

The experimental results are shown in Fig. 6 in which surface temperature was plotted as a function of time on a semi logarithmic graph. Except the anionic emulsion, the surface temperature of CNTs-emulsion composites increased with time, indicating that microwave was absorbed by those composites.

3.7 Strong points of CNTs-asphalt emulsions

The above-mentioned results clearly show that CNTs are potential filler for reinforcing as well as for giving microwave-absorbing property to conventional asphalt. This is probably the first study about CNTs-asphalt emulsions. Asphalt emulsions, of which viscosity can be easily controlled by the addition of surfactants, are a suitable binder for asphalt pavement.

Civil engineering structures of many countries need to renew old facilities. To renew of civil structures, it has been proposed that the implementation of new paving materials and methods ought to be adopted for performance enhancement and life cycle extension. The present study suggests that microwave heating to lower asphalt viscosity for partial repairs may be a promising construction technique. This will contribute to the ease of pavement construction, improvements in safety, and asphalt heating energy reduction. Thus, CNTs-asphalt emulsions will be greatly useful for construction fields.

4. CONCLUSIONS

The main conclusion to be drawn from the above results is as follows.

(1) In order to take advantage of the essential functions of the CNTs involved in asphalt, the CNTs should be dispersed into asphalt emulsions.
(2) As for both nonionic and anionic asphalt emulsions, as-prepared CNTs easily dispersed. For cationic emulsions, however, as-prepared CNTs failed to disperse. This problem was managed to solve by pretreating the CNTs with the acid solution and adding incrementally the pretreated CNTs.
(3) The CNTs-asphalt composites showed not only higher stiffness (higher performance in the penetration test) than carbon black-asphalt composites but also a new function, namely, the ability of microwave absorption, when compared under the same conditions (mass concentration of the each carbon material, measuring method, etc.).

5. ACKNOWLEDGMENT

A part of this study was supported by Grants-in-Aid for Young Scientists (B), JSPS (No.23760401).

6. REFERENCES

[1] Manzur T, Yazdani N. “Strength Enhancement of Cement Mortar with Carbon Nanotubes Early Results and Potential” Transportation Research Record, No.2142, 2010, pp.102-108.
[2] Shirakawa T, Tada A, Okazaki N, Iwahashi T, Kohata N. “Development of Construction Materials Using Advanced Nanocarbon Provided in a Hydrogen Manufacturing Process Subsidiary” Journal of JSCE Global Environment Engineering Research, Vol. 18, Aug.2010, pp. 81-88.(in Japanese)
[3] Wu Z, Chen1 Z, Du X, Logan J M, Sippel J , Nikolou M, Kamaras K, Reynolds J R, Tanner D B, Hebard A F, Rinzler A G. “Transparent, conductive carbon nanotubes films”, Science, Vol.305, Aug. 2004, pp.1273-1276.
[4] Tada A, Matsunaga T, Okazaki N. “Direct methane reforming process and its applications”, Transactions of the Materials Research Society of Japan, Vol.33, No.4, Dec. 2008, pp. 1059-1062.
[5] Aema, MS-19 Basic Asphalt Emulsion Manual, Asphalt Institute, 2008.
[6] Gridley P F, Vallerga B A. “Carbon black reinforcement of asphalts in paving mixtures”, ASTM Special Technical Publications, No.724, 1980, pp.110-128.
[7] Yamaguchi K, Sasaki I, Nishizaki I, Meiarashi S, Moriyoshi A. “Effects of film thickness, wave-length, and carbon black on photo degradation of asphalt”, Journal of the Japan Petroleum Institute, Vol.48, No.3, 2005, pp.150-155.

International Journal of GEOMATE, March, 2012, Vol. 2, No. 1 (Sl. No. 3)
MS No. 3q received August 31, 2011, and reviewed under GEOMATE publication policies.

Pertinent discussion including authors' closure, if any, will be published in the March 2013 if the discussion is received by Sept. 2012.
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