Transactions of the Materials Research Society of Japan 24 [3] 505-508 (1999)

Preparation of new organic-inorganic nanocomposites by the reaction of $Zn(OH)_2$

Kazutaka Fujita, Sumikazu Ogata, Hideyuki Tagaya, Jun-ichi Kadokawa, Masa Karasu, Koji Chiba

Faculty of Engineering, Yamagata University, Jonan, Yonezawa, yamagata, 992-8510 JAPAN
Fax:81-(0)238-26-3413, e-mail:tn168@dip.yz.yamagata-u.ac.jp

New organic-inorganic nanocomposite was obtained by the reaction of $Zn(OH)_2$ with isonicotinic acid. The interlayer spacing of the new composite was 1.07nm. The product was fibrous compounds which were confirmed by SEM images. Furthermore, by adding organic compound obtained nanocomposite the preparation of new aggregated fibrous compounds were confirmed in which non-covalent bonds between fibrous compounds were important.

Key words: organic-inorganic nanocomposite, fibrous compound, new aggregated fibrous compound , non-covalent bond

1.INTRODUCTION

We have already reported that the reaction of $Zn(OH)_2$ with organic carboxylic acid gave organic-inorganic nanocomposites by self-assembly reaction. The reaction product was fibrous layered compound, when organic compounds were bulky. In this study we prepared surface modified inorganic layer compounds by the reaction of $Zn(OH)_2$ with isonicotinic acid. And obtained compound were reacted with organic compound to attain interaction between nanocomposites.

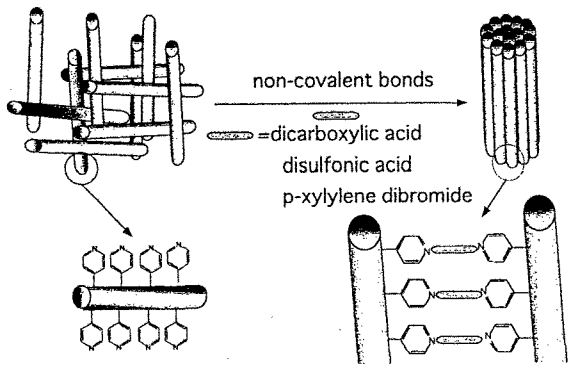


Fig.1 Preparation of organic-inorganic nanocomposite with non-covalent bond.

2.EXPERIMENTAL

2.1.Preparation of $Zn(OH)_2$

$Zn(OH)_2$ was prepared by the following method. A solution containing $Zn(NO_3)_2 \cdot 6H_2O$ in deaerated water was added over 0.5 h to stirred deaerated water containing NaOH at 277K.The reactant was filtered and washed. The resulting white solid was dried at 333K.

2.2.Preparation of fibrous compound and new aggregated fibrous compounds

$Zn(OH)_2$ and isonicotinic acid were reacted at 333K for 5h in water.After the reaction, the product was filtered and washed with water to remove unreacted acid. After then the product was dried under reduced pressure. Prepared product was reacted with dicarboxylic acid, disulfonic acid or p-xylylene dibromide at 333K for 5h in acetonitrile(ACN). After the reaction,the product was filtered and washed with ACN to remove unreacted acid. After then the product was dried under reduced pressure.

2.3.Characterization

X-Ray powder diffraction (XRD) data were collected on a Rigaku powder diffractometer, using CuK α radiation at 40kV and 20mA between 1.8 and 50° .FT-IR spectra were recorded on samples pressed into KBr disks using a Horiba FT-200. Thermal analyses (TG/DTA) of samples were performed on a Seiko SSC5000 thermal analysis system (heating rate:10K/min, in the flow of N_2).The morphology and microstructure of the samples were examined using a scanning electron microscope.

3.RESULTS AND DISCUSSION

3.1 Preparation of organic-inorganic nanocomposite

The XRD patterns of $Zn(OH)_2$ and reaction product of $Zn(OH)_2$ with isonicotinic acid are shown in Fig.2. New peaks in XRD appeared by the reaction with isonicotinic acid as shown in Fig.2(b). The d value of the reaction product of $Zn(OH)_2$ with isonicotinic acid was 1.07nm suggesting that the product was not zinc isonicotinate and isonicotinic acid. The IR spectra of $Zn(OH)_2$ and the reaction product of $Zn(OH)_2$ with isonicotinic acid were shown in Fig. 3. OH absorption at near 3500cm^{-1} for $Zn(OH)_2$ fairly decreased by the reaction with isonicotinic acid and new absorption peaks at near 1630cm^{-1},1550cm^{-1} and 1390cm^{-1} appeared. The peaks at 1550cm^{-1} and 1400cm^{-1} were assigned to the symmetric stretching

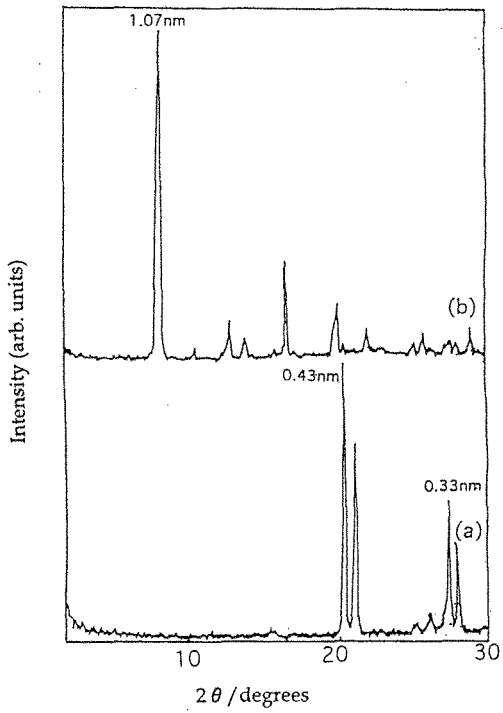


Fig.2 XRD patterns of (a) $Zn(OH)_2$, and the reaction products of $Zn(OH)_2$ with isonicotinic acid.

vibration of carboxylate. These two peaks indicate the formation of COO-Zn bond. The peak at 1625cm^{-1} was assigned as expansion and contraction vibration absorption of pyridine ring. The IR absorption peaks of isonicotinic acid were not observed. These results indicate that $Zn(OH)_2$ reacted with isonicotinic acid giving organic-inorganic nanocomposite in which isonicotinic acid reacted with Zn-OH giving RCOO-Zn bond. The thermal behavior of $Zn(OH)_2$, isonicotinic acid and obtained organic-inorganic nanocomposite were measured by TG/DTA. 13% weight of $Zn(OH)_2$ decreases up to 393K,suggesting the evolution of absorbed water. TG analysts of isonicotinic acid alone shows weight that loss occurred at between 430 and 580K. In contrast, weight loss of the reaction product of $Zn(OH)_2$ with

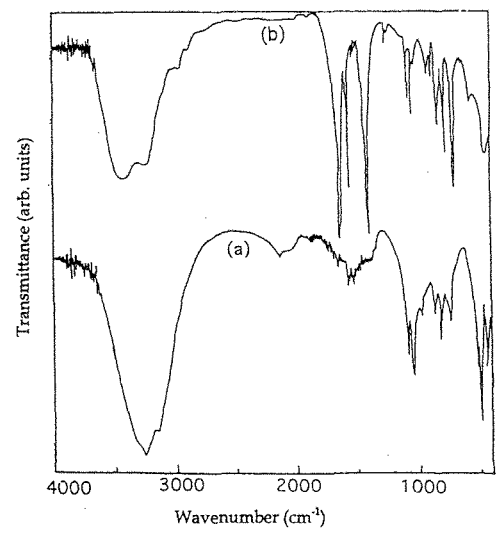
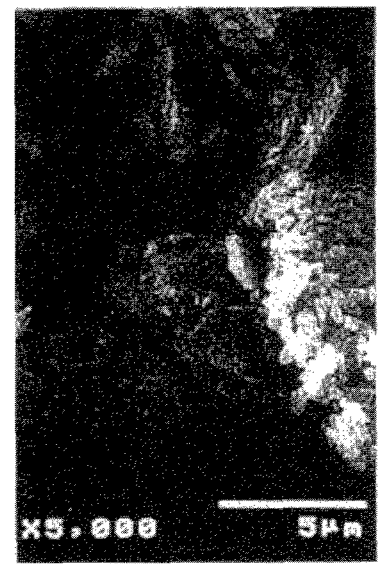


Fig.3 IR spectra of (a) $Zn(OH)_2$, and the reaction products of $Zn(OH)_2$ with (b) isonicotinic acid.

(a)



(b)

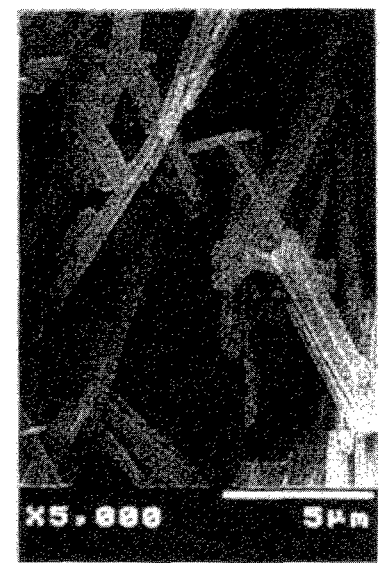


Fig.4 SEM images (5000×magnification) of (a) $Zn(OH)_2$, and (b) the reaction product of $Zn(OH)_2$ with isonicotinic acid.

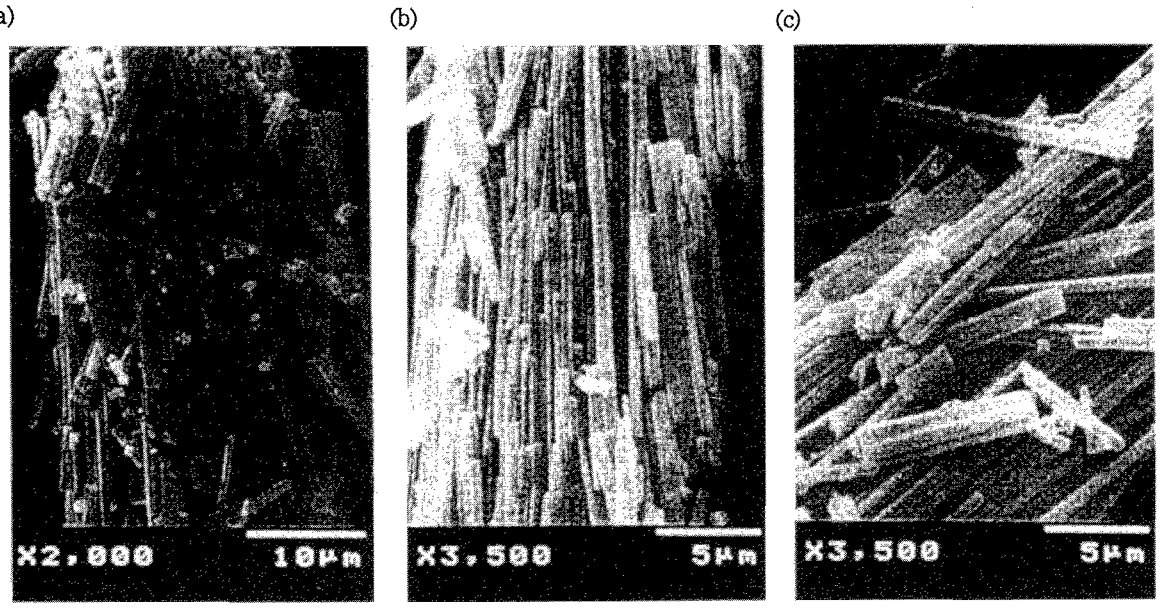


Fig.5 SEM images (2000×magnification) of (a) the reaction product of organic-inorganic compound with malonic acid, (3500×magnification) of (b) the reaction product of organic-inorganic compound with 1,2-ethanedisulfonic acid, (c) the reaction product of organic-inorganic compound with p-xylylene dibromide.

isonicotinic acid was observed at between 630~720K, and were more thermally stable than that of isonicotinic acid. CHN elemental analyses gave,empirical formula represented as $Zn(OH)_{1.27}(-OOC\text{-}C_5H_4N)_{0.73}$ indicating that 37% of OH groups reacted with isonicotinic acid. SEM images indicating the microstructures of $Zn(OH)_2$ and obtained organic-inorganic nanocomposite were shown in Fig.4. Although $Zn(OH)_2$ was plate-like structure, obtained organic-inorganic nanocomposite was fiber-shape structure.

3.2.preparation of aggregated compounds with non-covalent bond

Obtained fiber-shape nanocomposite was further treated in various compound to organize by non-covalent bonds. SEM image showed that no morphology change occured by stirring the reaction product of $Zn(OH)_2$ with isonicotinic acid in ACN. Dicarboxylic acid, disulfonic acid or p-xylylene dibromide was added to the reaction

Table 1 Preparation of aggregated compounds with non-covalent bonds between fibrous compounds

reagent	Morphology	total size(μm)
malonic acid(2times)	bundle	29.0
succinic acid(2times)	bundle	18.9
succinic acid(20times)	plate-like	-----
glutaric acid(2times)	bundle	16.3
fumaric acid(2times)	bundle	30.7
didodecanoic acid(2times)	bundle	32.1
1,2-ehanedi-sulfonic acid(2times)	bundle	17.1
p-xylylene di-bromide(2times)	bundle	22.6
none	fibrous	not found

product of $Zn(OH)_2$ with isonicotinic acid. SEM images showed that of the organized nanocomposite were shown in Fig.5. Dicarboxylic acid, disulfonic acid ,or p-xylylene dibromide was added to the reaction product of $Zn(OH)_2$ with isonicotinic acid. SEM images showed that of the organized nanocomposite were and p-xylylene dibromide acted to assemble fiber-shape nanocomposites. When excess amount of succinic acid was add,fiborus compound changed to plate-like structure as shown in Table1. This result suggested that succinic acid reacted with remained hydroxyl group of $Zn(OH)_2$.

It is note worthy that by adding organic compound to fibrous compound, new aggregated fibrous compounds were obtained in which non-covalent bonds between fibrous compounds might be important..

REFERENCES

1. S. Ogata, H. Tagaya, J. Kadokawa, M. Karasu and K. Chiba transactions of the Materials Research Society of Japan. Vol.20
2. S. Ogata, Y. Tasaka, H. Tagaya, J. Kadokawa and K. Chiba *Chemistry Letters* 1998
3. E. Capaigne, W. Meyer Contribution No.1048
4. T. Kato, Jean M. J.Frechet *J.AM.Chem.Soc.*,**111**,8533-8534(1989)

(Received December 11, 1998; accepted January 18, 1999)