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Hybridization of cellulose nanofiber with amine-polymers and its ability on sick house syndrome gas decomposition



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ABSTRACT

As an environment-conscious catalyst, a nanocomposite of Pt nanoparticles supported by dendrimer and cellulose nanofiber was designed. The poly(amido amine) dendrimer was immobilized, by the amidation reaction, on the 2,2,6,6-tetramethyl-1-piperdinyloxy free radical oxidized cellulose nanofiber (TOCNF), and its binding ratios at different mixing ratios were colorimetrically analyzed. The results showed that the dendrimer bound on TOCNF caused a saturation, while polyethyleneimines (PEIs) almost linearly increased the binding mass ratio per TOCNF as the mixing ratio rose. The dendrimer/TOCNF formed a viscoelastic gel in wide mixing ratios, while the PEIs/TOCNF varied their gel characters depending on molecular weight of PEI and mixing ratio. The Pt nanoparticle-incorporated dendrimer (DENPtNPs) was chemically bound on TOCNF. The TOCNF/DENPtNPs gels were dried to form solid films, and then applied for the decomposition of formaldehyde in gas phase. It was demonstrated that the dendrimer effectively captured formaldehyde and the PtNPs decomposed it. These results would be useful to develop catalytic nanocomposite membranes.

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1. Introduction

Generically, the large specific surface area of materials improves the chemical reactivity [1,2]. Therefore, nanomaterials are preferably used as catalysts and their supports [2]. Metallic nanoparticles, typically Pt nanoparticles, have been examined for various reactions with support of the nano-sheets and nano-fibers such as graphene and carbon nanotubes (CNTs) [3–9]. In our previous works, nanoparticles were synthesized with dendrimers, and covalently immobilized on oxidized CNTs via the amidation reaction between amine groups in dendrimers and carboxyl groups on CNTs [10–16]. These nanocomposites could be used as effective catalysts and sensing devices. However, the use of CNT's family could be troublesome because of their potential hazardousness, and safe nano-materials are strongly desired [17].

In this decade, the cellulose nano-fibers (CNFs) are gathering attentions in the material science because of their mechanical properties and environmental suitability [18,19]. In particular, the 2,2,6,6-tetramethyl-1-piperdinyloxy free radical (TEMPO)-oxidized

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CNF (TOCNF) is the ultrafine fiber and have many carboxyl groups on its surface, which are suitable for the chemical modifications [19]. Thereby, the TOCNF can be applied to the support of catalysts. From this viewpoint, we have examined the modifications of TOCNF to develop catalysts and absorbers [20–24]. It was demonstrated that the nanocomposites of nanoparticle/dendrimer/TOCNF allowed the diffusion of small molecules in their matrix, although the simple TOCNF formed a film with powerful gas-barrier function [23,25]. Thus, the availability of these nanocomposites for catalysts and absorbers were verified; however, the detailed structures of these nanocomposites were not yet confirmed.

In this study, the hybridization of dendrimer and TOCNF was investigated, and the films prepared from gels of Pt nanoparticle/dendrimer/TOCNF nanocomposites were used to decompose formaldehyde, which is the main cause of the sick house syndrome [26]. The adsorption behavior of formaldehyde on each component in the nanocomposites was analyzed, too. These results would be useful for further development of environmentally compatible catalysts, which could be suitable for domestic applications.

2. Experimental section

2.1. Materials

Never-dried pulp was prepared from a wood powder (Populus, sp., Sanko Co., Japan, and Eucalyptus, sp. Chung Hwa Pulp

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Corporation, Taiwan) by the dewaxing process using the Soxhlet extraction (toluene/ethanol=2:1 v/v) and by the delignification process [18]. Fourth generation (G4) poly(amido amine) dendrimer (PAMAM DEN) with NH₂ terminals (10 wt% in methanol, molecular weight 14,213), polyethylenimine (PEI) (50 wt% in water, Mn 1200, Mw 1300; Mn 10,000, Mw 25,000; and Mn 60,000, Mw 760,000), and fluorescein isothiocyanate (FTIC) were purchased from Sigma-Aldrich. TEMPO, sodium hexachloroplatinate hexahydrate (98%), an aqueous formaldehyde solution (37 wt%), and pentane-2,4–dione solution (99%) were purchased from ACROS organics. Other chemicals used were of analytical grade and used without further purification. The ultrapure water (18.2 M Ω cm) was obtained from a Yamato Millipore WT100.

2.2. Instruments

The ultrasonication was carried out with an ultrasonic processor (Q700, Misonix, USA) equipped with a half-inch tip. The treatment was performed in an ice-cooled bath. The ultravioletvisible (UV-VIS) absorption spectra were measured at a scan speed of 200 nm/min and the wavelength number ranged from 200 to 1200 nm on a UV-VIS spectrophotometer (V-670, Jasco, Japan). The hybrid of TOCNF and polymers was filtrated by membrane filter (cellulose acetate, 0.2 µm pore) before the measurement. The concentrations of polymers in the filtrate were respectively calculated by the calibration curve method using the FITC-labeled polymer solutions known as the standards. AFM observation was performed with a Digital Instruments NanoScope III, Veeco. The dispersion was spread on a freshly-cleaved mica substrate by a spin-coater. Transmission electron microscopic (TEM) images were produced by a Hitachi H-7000 instrument, operated at 100 kV. Thermogravimetric analysis (TGA) of powders was performed using a TGA Q500 instrument (TA Instruments) under an atmosphere of air and N_2 with a heating rate of 10 °C/min.

2.3. Preparation of TOCNF nanofiber and its hybridization with amine-polymers

The TOCNF was prepared from the never-dried pulp as previously reported [19–25]. Typically, never-dried pulp (1.0 g), KBr (119 mg), and TEMPO (15.6 mg) were dispersed in water (100 ml). To this dispersion, an aqueous solution of NaClO (2.86 g, 13 wt%) was added with stirring, and the pH was controlled to 10. Since the pH decreased as the reaction proceeded, the pH was maintained at 10 by adding an aqueous NaOH solution (0.5 N) until the change in pH became negligible after 24 h (see supporting information Figs. S1 and S2). Thus-obtained TEMPO-oxidized pulp was washed with water by centrifugation (6000 rpm, 5 min) till the pH of supernatant became 7. The purified TEMPO-oxidized cellulose pulp (2.0 g as dry weight) was suspended in of water (100 ml), added NaBH₄ (1 g), and stirred for 8 h to reduce aldehyde groups (see supporting information Fig. S3). After the reduced TEMPO-oxidized cellulose pulp was washed with water by centrifugation, it was dispersed in water to be 0.2 wt% of dry weight and subjected to the ultrasonication for 40 min to obtain TOCNF.

For quantitative assay, the amine-polymers were labeled by FITC. FITC (15.6 mg) was dissolved in an aqueous solution of NaHCO₃ (40 ml, 100 mM) at 0 °C. The methanol solution of dendrimer (0.1421 g of dry weight) and PEIs (0.368 g of dry weight) were diluted to 5 ml by the solution of NaHCO₃ (100 mM). These solutions of polymers were cooled to 0°C, and quickly mixed with the FITC solution (2 ml for the dendrimer solution and 10 ml for the PEI solutions) in the ice-cooled bath. Finally, the volume of solutions was adjusted to 20 ml by the solution of NaHCO₃ (100 mM) and left overnight to accomplish the reaction.

For the hybridization, an aqueous dispersion of TOCNF (0.2 wt%) was adjusted to pH 10 with NaOH and cooled in the ice bath. To the dispersion (5 ml), condensation reagents, EDC/NHS (5 mg, respectively), were dissolved. After 1 h, the appropriate amounts of the solution of FITC-labeled polymers were added into the dispersion of TOCNF, and the reaction mixture was then diluted to 10 ml with the ice-cooled solution of NaHCO₃ (100 mM). The reaction mixture was left at room temperature.

2.4. Hybridization of TOCNF with platinum

nanoparticles-encapsulated dendrimer-(DENPtNPs) and preparation of hybrid films

Nanoparticles-encapsulated dendrimer (DENPtNPs) was prepared as previously reported [10–16]. Briefly, Na₂PtCl₆ \cdot 6H₂O was added into an aqueous solution of PAMAM dendrimer at the mixing ratio of [Pt-precursor]: [NH₂ group in dendrimer]=0.2: 1 or 0.5: 1. The solution adjusted at pH 4 was stirred for more than 24 h. Then, an aqueous 0.3 M NaOH solution of a reducer, NaBH₄, was mixed with the dendrimer-Pt precursor solution at the mixing molar ratio of reducer: Pt-precursor (NaBH₄: Na₂PtCl₆·6H₂O) at 1:1, and the mixed solution was stirred for 1 day and kept at room temperature.

The cross-linkage between TOCNF and DENPtNPs was accomplished using the coupling reaction [20–24]. Equimolar mixture of EDC and NHS were added to TOCNF dispersion at pH 10. Then, an EDC-activated carboxylate group in TOCNF reacted with NHS to form a stable NHS carboxylate. After 1 h, the reaction solution was mixed with an aqueous solution of DENPtNPs to be the molar ratio of 1:1:1 (EDC:NHS: dendrimer), and then the NHS-carboxylate was combined with the terminal amino group of dendrimer.

The gelled solution of TOCNF/DENPtNPs was filtered under reduced pressure using a cellulose acetate membrane (pore size: $0.2\,\mu$ m) until the film is formed, and then the wet film was dried overnight. This method is called the "filter-method" and the film is called the "filtered-film". On the other hand, the other preparation of film by the natural air dry in the chamber is called the "dried-method", and the film is called the "dried-film". The obtained films were used for characterizations.

2.5. Quantification of HCHO on TOCNF/DENPtNPs films

Colorimetric agent (CA solution) was prepared by dissolving ammonium acetate (15 g) in water, and then adding acetic acid (0.3 ml) and acetylacetone (0.2 ml). The mixture was diluted with water to become total 100 mL of the CA solution. The film (TOCNF, TOCNF/DEN or TOCNF/DENPtNPs) was held up on an aqueous HCHO solution (20 ml) in the reactor vessel, and the closed vessel was heated to around 70 °C [27]. The reaction was carried out for 0.5, 1.5, 3, and 4 h, and then the film was immersed into water (10 ml) for 1 h, half of which was mixed with a CA solution (5 ml). Every mixed solution was subsequently shaken for around 15 s and kept for 30 min in a thermostatic water-bath at 40 °C, followed by cooling for 30 min at room temperature. Absorbance measurements were carried out afterwards using a 1 mm quartz cell. The blank solution used for the baseline measurement was a water: CA (1:1 v/v) solution.

3. Results and discussion

3.1. Characterization of TOCNF

The transmittance spectra of TOCNF dispersions before and after the reduction reaction were shown in Fig. 1. The high transmittance (>80%) of both dispersions in the visible range was



Fig. 1. Optical extinction spectra of TOCNF dispersions before and after the reduction reaction.



Fig. 2. An AFM image (right) and its sectional analysis (left) of TOCNF spread on a mica surface.

consistent with the translucent appearance of dispersions, suggesting that the pulp was fibrillated to the nanofibers. The obtained TOCNF was observed by AFM (Fig. 2). The height of nano-fiber was around 3 nm, which agreed with the literature values [19].

3.2. Hybridization of amine-polymers with TOCNF

TOCNF was hybridized with PAMAM dendrimer and PEI, which was classified by the molecular weight; the low-MW (Mw 1300), medium-MW (Mw 25,000), and high-MW (Mw 760,000) PEI. Before the hybridization, the polymers were labeled with the FITC at the mixing ratio of 1/320 per primary and secondary amine in polymers: The number of amines in PEI was calculated with the estimation that the ratio of primary, secondary, and tertiary amines was 1:2:1 [28]. Since the ratio of FITC per amine was significantly small, the FITC-labeling on polymers was considered not to affect the hybridization with the TOCNF.

The polymers were mixed with the TOCNF at an alkaline condition (pH ~10), where the amine groups in polymers were not significantly protonated [29,30] and then the mixture was homogeneously prepared. On the other hand, the mixing at lower pH resulted in the immediate gelation via the electrostatic interaction between amines in polymers and carboxyl groups in TOCNF, and the reaction system became inhomogeneous. Since by means of condensation reagents (EDC and NHS), the TOCNF and the polymer were cross-linked by the amidation reaction, the mixture gradually increased its viscosity as the reaction proceeded, and then formed a clear gel after 2-3 h.

The binding ratio of polymers on TOCNF was calculated from the absorbance at 494 nm (see supporting information Figure S4A), which corresponded to an absorption band of fluorescein



Fig. 3. (A) Mass ratios and (B) number binding ratios of polymers bound on TOCNF against mixing ratio of polymers per TOCNF (mass ratio (w/w)) (number binding ratio (mol/unit mol)).

chromophore (Eq. (1)).

$$B = 1 - \frac{A_{\text{filtrate}}}{A_{\text{control}}} \tag{1}$$

where *B* is binding ratio, A_{filtrate} is absorbance of filtrate, and the A_{control} is absorbance of TOCNF/FITC-labeled polymers dispersion. The binding ratios of the polymers per TOCNF were plotted against the mixing ratio of polymers per TOCNF (see supporting information Fig. S4B). From these values, the mass ratios of polymers per TOCNF (R_{mass}) and the number binding ratios (number of polymer molecule per carboxyl group: R_{mol}) were also calculated by Eqs. (2) and (3), respectively, and plotted in Fig. 3.

$$R_{\rm mass} = BR_{\rm mix} \tag{2}$$

$$R_{\rm mol} = 1000BR_{\rm mix}/{\rm MnC_{\rm acid}} \tag{3}$$

where R_{mix} is the mixing ratio, Mn is the number-average molecular weight of polymer, and C_{acid} is the concentration of carboxyl group in TOCNF, which was given as 1.2 mmol/g (see supporting information Fig. S2).

As seen in Fig. S4B, the binding ratio of dendrimer was the highest at the low concentration and decreased as the mixing ratio increased. Meanwhile, the mass ratio was saturated at 0.42 at the mixing ratio of 0.6 (see Fig. 3A), but the number binding ratio was \sim 0.025 (see Fig. 3B), suggesting that a dendrimer molecule bound per \sim 40 carboxyl groups. Since the dendrimer molecule has a spherical structure with 64 primary amines in periphery, this number binding ratio suggests that the dendrimer was loosely packed or flatting on a TOCNF. Otherwise the dendrimer cross-linked the TOCNFs. The rigid TOCNFs could likely entangle by themselves but effectively develop the network structure by the cross-linking to cause a gelation [30–33].

On the other hand, the binding ratios of PEI on TOCNF depended remarkably on molecular weight of PEI: The increasing binding ratio with mixing ratio of low-MW PEI (Fig. S4B) resulted in the rapid increasing of the mass ratio and the number binding ratio (Fig. 3A), which suggest that the low-MW PEI flexibly changed its conformation from the flatly adsorbed one to the perpendicularly expanded one on TOCNF as the mixing ratio rose. Meanwhile, the binding ratios were almost constant for the medium-MW PEI and slightly decreased for the high-MW PEI as the mixing ratio increased (Fig. 34B). Then, the mass ratios and the number binding ratios of both PEIs almost lineally increased (Fig. 3). These behaviors indicate that the conformational changes in PEI molecules were suppressed as the molecular size increased because of their large steric hindrance.

Fig. 4 shows the aspect of gels of TOCNF/FITC-labeled polymers after amidation reaction prepared at different polymer/TOCNF ratios (w/w). The dendrimer/TOCNF nano-composites formed stable viscoelastic gels in all the mixing ratios in this study (from 0.1 to 1.0 w/w). However, the gels of PEI/TOCNF nano-composites varied their properties with the mixing ratio and the molecular weight of



Scheme 1. Gelation mechanisms of TOCNF/amine-polymers composites. (A) TOCNF without amine-polymer, (B) TOCNF/dendrimer, (C) TOCNF/low-MW PEI at low mixing ratio, and (D) TOCNF/medium-MW and high-MW PEIs.



Fig. 4. Photos of TOCNF/FITC-labeled polymers after amidation reaction. The mixing ratios (w/w) of polymer/TOCNF were indicated on the photos.

PEIs. The low-MW PEI formed a stable viscoelastic gel at the low polymer/TOCNF ratio, but the viscoelastic behavior of PEI/TOCNF composites weakened at high ratio or for medium-MW PEI. The high-MW PEI resulted in the liquid-liquid phase separation at low ratio. These behaviors could be explained by the difference in network structure of gels (Scheme 1): Since the molecules themselves of dendrimer and low-MW PEI have compact structures, the characteristics of hybridized gel were mainly regulated by the network of TOCNF, although they contribute as a linker for the formation of viscoelastic gel. On the other hand, the PEIs of higher content or bulky-shape (medium-MW and high-MW PEIs) could decrease a role as a linker by the capping of TOCNF with polymers and display the weakening of the gel elasticity. Especially, high-MW PEI molecules occupy the void volume in the network of TOCNF even at low polymer content and thus solvent (water) will be phase-separated from composite gel phase.

3.3. Characterization of TOCNF/DENPtNPs films

The Pt nanoparticles encapsulated in PAMAM dendrimer were produced by the reduction of hexachloroplatinate [10–16]. The TEM images of DENPtNPs synthesized at different unit mole ratios (0.2:1 and 0.5:1) of Pt precursor and amine terminal group of dendrimer are compared in Fig. 5A. The images indicate that PtNPs of around 3 nm size are homogeneously dispersed at the condition of 0.2:1 ratio, but the PtNPs nanoparticles prepared at 0.5:1 ratio were agglomerated. On this condition, the concentration of the



Fig. 5. (A) TEM images of DENPtNPs at different ratios (0.2:1 and 0.5:1) of Pt precursor and NH₂ terminal group in dendrimer. (B) TEM images of TOCNF at different carboxylate contents (0.86 and 1.74 mmol/g). Inset is photographs of the dispersions. (C) UV-vis transmittance of TOCNF films at carboxylate contents of 0.86 and 1.74 mmol/g. (D) TGA results of a TOCNF/DEN(PtNP)s film.

dendrimer is not enough high to protect and stabilize the PtNPs in the medium.

Here the TOCNF dispersions were prepared at different carboxylate contents by changing the cellulose concentration in the TEMPO oxidation reaction. As seen in Fig. 5B (inset), the TOCNF dispersion at 1.74 mmol/g of carboxylate was more transparent than that at 0.86 mmol/g. Similar difference was observed even on the transmittance behavior of the TOCNF films, which were prepared by the filtration method from the TOCNF dispersions. The transmittance profile of the films (Fig. 5C) indicated enough light transmission of TOCNF films at wavelengths above 400 nm as well as the transmission of the TOCNF dispersions (Fig. 1). However, the TOCNF film with high carboxylate content displayed high transmittance, because high carboxylate content produces enough electrostatic repulsion between cellulose nanofibers to release their agglomeration. The substantial dispersion of TOCNF in water was confirmed from TEM images in Fig. 5B: TOCNF fibrils at 1.74 mmol/g were homogeneously dispersed with same fibril



Fig. 6. (A) HCHO amounts adsorbed on (a) TOCNF, (b) TOCNF/DEN and (c) TOCNF/DENPtNPs films as a function of HCHO concentration in reactor. The reaction time is 1.5, 3 and 4 h. [Pt precursor]: [NH2 group in dendrimer] is 0.5:1. (B) (C) HCHO amounts adsorbed on TOCNF and TOCNF/DEN films and decomposed on TOCNF/DENPtNPs as a function of HCHO concentration in reactor and of time period, respectively. They are denoted as (a) TOCNF, (b) DEN and (c) PtNPs, respectively.

thickness, but the fibrils at 0.86 mmol/g still remained bundles of fibrils. Thus, the concentration of 1.74 mmol/g was utilized for the preparation of TOCNF/DENPtNPs composites and their films. The TOCNF/DENPtNPs formed the viscoelastic gels, as mentioned in 3.2, and the homogeneous immobilization of DENPtNPs in the gel network was suggested.

Fig. 5D shows the TGA curves of TOCNF/DENPtNPs. The TGA profile indicated triple weight drops by removal of adsorbed water at the temperature below 100 °C, by decomposition of organic components at 220–340 °C and by decomposition of remaining organic components at 550–580 °C. The residue at high temperature above 580 °C is metal Pt, amount of which was about 10 wt%.

3.4. Capture and decomposition of HCHO in TOCNF-based films

The capture and decomposition of HCHO was carried out on TOCNF, TOCNF/DEN and TOCNF/DENPtNPs films. The quantification of HCHO remained on films was performed by calorimetric method based on the calibration curve of a UV-VIS absorption band on reaction of CA with HCHO based on Hantzsch reaction [34]. Although CA does not have color (no absorption band at visible wavelength region), the reaction product, 3,5-diacetyl-1,4-dihydrolutidine, displays yellow color by an absorption band at 413 nm.

While TOCNF has a binding site on TOCNF and TOCNF/DEN exhibits additional binding site on dendrimer, TOCNF/DENPtNPs possesses catalyst for the decomposition of HCHO besides the binding sites. The expected catalysis of HCHO is the oxidation to CO_2 and H_2O through HCOOH [35]. Then, HCHO adsorbed onto the catalytic active site of DEN(PtNP)s. At the active site is oxidized.

Fig. 6A shows the profile of HCHO adsorption on the TOCNF, TOCNF/DEN and TOCNF/DEN(PtNP)s films, which were exposed on HCHO solutions of different concentrations in the reactor for different time period (1.5, 3 and 4 h). The adsorption on TOCNF film was independent of the HCHO concentration but the adsorption on films including dendrimer and DENPtNPs depended on the HCHO concentration. Moreover, the adsorption of HCHO on a TOCNF/DENPtNPs film was always lower than the adsorption on a TOCNF/DEN film. This indicates that the adsorption of HCHO is limited on TOCNF but HCHO can adsorb much more on dendrimer and DENPtNPs, and the coexisting Pt nanoparticles should decompose the adsorbed HCHO gas.

To quantify the amount of HCHO on three binding moieties of TOCNF, dendrimer and DENPtNPs, the data in Fig. 6A was recalculated and replotted on Fig. 6B as a function of HCHO concentration in reactor and Fig. 6C as a function of time period of the adsorption, where the HCHO concentration indicates the amounts of HCHO on TOCNF, the amounts of HCHO on dendrimer calculated as [HCHO on DEN] = [HCHO on TOCNF/DEN] – [HCHO on TOCNF] and the amounts of HCHO decomposed by PtNPs as [HCHO on PtNPs] = [HCHO on TOCNF/DEN] – [HCHO on TOCNF/DENPtNPs].

The results indicate that the adsorption of HCHO on the TOCNF film did not notably change with the variation of HCHO concentration and time interval because of the saturation of the binding site on TOCNF by HCHO. Contrarily, the adsorption of HCHO on dendrimer moiety increased with reaction time and HCHO concentration in reactor, indicating the preferable absorption ability of dendrimer on HCHO adsorption, which is driven by the encapsulation of HCHO in voids in dendrimer molecule [23]. Whereas, the decomposed amount of HCHO on the TOCNF/DENPtNPs film scarcely depended on HCHO concentration in reactor. This indicates that the Pt nanoparticles react as a catalyst independent of the total amount of adsorbed HCHO, since the catalytic reaction happens only near the catalysts. On the other hand, the decomposed HCHO amount by PtNPs decreased with increasing the reaction time. It can be assumed that products (CO_2 and H_2O) after catalytic reaction of HCHO should remain near catalyst and they may disturb the approach of the fresh HCHO molecule.

4. Conclusions

The TOCNF was hybridized with amine-polymers (PAMAM dendrimer and PEIs with different molecular weights). The hybrids formed transparent gels, and especially the dendrimer led to a homogeneous viscoelastic gelation in the wide range of mixing ratio. The number binding ratios of polymers per TOCNF suggested that the dendrimer partially covered the surface of TOCNF, facilitating the cross-linking, while the PEI could vary their conformations to cover the TOCNF at the different concentrations. DENPtNPs were chemically bound on TOCNF and the composites displayed effective catalytic behavior by decomposing formaldehyde gas adsorbed on dendrimer. This result indicates the possible application of the present catalyst-including TOCNF to diminish not only the causative gas of sick house syndrome but also any unexpected gases like endocrine disruptor and greenhouse effect gas.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtice.2018.02.003.

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