〔高度技術教育研究センター〕

〔区 分 A〕

Optochemical sensor for HC1 gas based on tetraphenylporphyrin dispersed in styrene-acrylate copolymers : Effects of glass transition temperature of matrix on HCl detection

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Sensors and Actuators B, vol.85, pp197 — 204, (2002) .

The spectral changes of tetraphenylporphyrin ($\mathrm{TPPH_2}$) -Polyrner composites in the visible region were examined in order to detect HCl gas. For $\mathrm{TPPH_2}$, the absorbance of the Soret and Q bands were sensitive to ppm levels of HC1.The sensing mechanism were characterized basing the protonation reaction and sorption isotherm: $\mathrm{TPPH_2 + 2HCl_{film} \Leftrightarrow TPPH_4^{2+} \cdot 2CI^-}$and $[\mathrm{HCl^{film}}] = a\,[\mathrm{HCl_{gas}}]^n$. The equilibrium constant of the former was decreased with increase in the working temperature and in glass transition temperature (Tg) of polymer matrix. The number of active sites (a) fot HCl sorption decreased with a decrease in the Tg. The response behavior was improved by using polymer with lower Tg.

Prparations of perovskite-type oxides $\mathrm{LaCoO_3}$ from three different methods and their evaluation by homogeneity, sinterability and conductivity

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Solid State lonics, vol.158(2003), p.133-139.

Perovskite-type oxide, $\mathrm{LaCoO_3}$, was prepared by three different methods which are based on the calcination of a mixture of $\mathrm{1/2La_2O_3}$ and CoO, the calcination of coprecipitates of $\mathrm{1/2La_2(C_2O_4)_3 \cdot nH_2O}$ and $\mathrm{CoC_2O_4 \cdot mH_2O}$ and the thermal decomposition of a heteronuclear complex $\mathrm{La[Co(C_2O_4)_3] \cdot 8.5H_2O}$. Thermogravimetric analyses and measurements of infrared spectra and powder x-ray diffraction patterns indicated that the formation of $\mathrm{LaCoO_3}$ is complete at 1000, 1200 and 600°C for the respective methods. The electron microprobe analyses showed that the homogeneity is the highest for $\mathrm{LaCoO_3}$ obtained from the complex decomposition method. The conductivities of $\mathrm{LaCoO_3}$ sintered at 1100—1500°C after the preparation by the heteronuclear complex decomposition were lower by about one order than those of $\mathrm{LaCoO_3}$ sintered from the mixture of $\mathrm{1/2La_2O_3}$ and CoO and the coprecipitates of $\mathrm{1/2La_2(C_2O_4)_3 \cdot nH_2O}$ and $\mathrm{CoC_2O_4 \cdot mH_2O}$, whereas the densities are similar to each other regardless of the preparation methods.

Polymer film produced by a marine bacterium

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Journal of Bioscience and Bioengineering, vol.95, NO.1, pp72-76, (2003) Biojelly® is a sort of polymer that is formed on a cellulose acetate membrane immersed in seawater. Interestingly, Biojelly® inhibits attachment of marine organisms such as algae and barnades. We could successfully isolate several marine microorganisms from Biojelly®-attached microorganisms.One of these isolates, strain SHY1-1, produced water-insoluble polymeric materials in natural seawater supplemented with yeast extracts and glucose. This strain was assigned to be *Alteromonas* sp. by the method of the 16S rRNA gene sequencing and phylogenetic analysis. Biojelly® and the polymer film produced by *Alteromonas* sp. SHY1-1 were qualitatively characterized by Fourier transformed infrared (FT-IR) spectroscopy and thin-layer chromatography(TLC). The result indicated that naturally occurring Biojelly® and the polymeric materials obtained in this work both were a sort of mucopolysaccharide consisting of amino sugars. In addition, the attachment assay with larvae indicated that both polymer films had similar anti-fouling activity against barnacle (*Balanus amphitrite*).

〔区 分 C〕

イルメナイト型$CoTiO_3$の酸化物混合法および錯体法による調製

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新居浜工業高等専門学校紀要、第39巻(2003)、p.41-44.

イルメナイト型酸化物$CoTiO_3$を2つの異なる調製法から作製した。CoOとTiO_2池の混合物を仮焼したもの(Co-Ti-O)および異核錯体$[CoNO_2(NH_3)_5][TiO(C_2O_4)_2]4H_2O$の熱分解物(Co-Ti-Complex)である。調製した前駆体の特性を、熱重量測定、赤外吸収スペクトル測定および粉末X線回折測定などによって検討した。$CoTiO_3$厚相の生成は、Co-Ti-Oが1000°C以上、Co-Ti-Complexが800°C以上で認められた。

〔区 分 D〕

キトサンを用いた低摩擦抵抗船底塗料の開発

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平成13年度地域新生コンソーシアム研究開発事業　成果報告書

キトサンの塗膜を作成するために、種々の化合物で誘導体を作成した。ラウリル基を付加し、グルタルアルデヒドで架橋したキトサン誘導体においては、同じ粗度を有する面と比較すると約10%摩擦抵抗を低減することが可能であるとの結果を得たレまた、全てのキトサン誘導体において、フィルム状および微粉末状のいずれにおいても天然海水および活性汚泥により適切な分解性を確認した。この時、架橋度や形状を変えることにより、分解性を制御できることも見出した。

〔区 分 E〕

Temporal Emission Characteristics of White Light-Emitting Diodes for High-Speed PulsedCurrent

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19th Congress of the International Commission for Optics, Fir6nze, Italy, 2002

Temporal emission characteristics of two kinds of white light-emitting diodes (LEDs), NSPW300BS (Nichia Co.)and E1S09-0W1AP-02 (Toyoda Gousei Co.), for high-speed repetitive pulsed current have been studied. The structure of the two LEDs are slightly different: The former utilizes fluorescence from YAG materials excited by a blue LED together with the blue LED light itself, white the latter utilizes that from some kinds of composite materials excited by an ultraviolet LED. Each LED was driven by a laboratory-made, nanosecond, high-current, pulse generator using an avalanche transistor. As was expected, the fluorescence decay times for the two LEDs were fairly different. The fluorescence decay time of the Nichia's LED was about 75.0 ns, while that of the Toyoda's LED was ranging from a several hundred nanoseconds to a few milliseconds depending on the emission wavelength. Introducing a time-resolved light-detection technique, the pulse-driven white LED appears useful for some kinds of sensor applications as a wavelength-variatble light source.

画像データによる透明樹脂部品欠損の自動判別法について

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電気学会研究会資料　産業計測制御研究会　IIC-03-74～81「ウェーブレットとその周辺技術」平成15年3月26日

本研究は, 円筒形透明樹脂部品の生産ラインに導入するための非接触欠陥検査システムにウェーブレット処理を適用することを目的とする。微少欠陥を有する円筒形透明樹脂部品の外周360度画像は, 多重解像度解析によりノイズ除去したあとの輝度を利用することにより, 線画として欠陥部が強調された1次元時系列データとして取り扱うことができる。我々は, この時系列データに連続Wavelet変換を行い, ゲイン情報, 位相|貴報を用いた特異点検出によりひび割れの位置が検出できることを見出した。1次元時系列にすることのメリットは, 生産ラインにおける検査において, 単に欠陥の有無を知るだけでなく, そのひび割れが工場の中のどの工程で発生したかというフィードバック情報を与えることとなり, 製品の動的品質管理を実現することができる可能性があるということである。動的品質管理をラインに導入すれば製品の品質管理を格段に向上させることが期待できる。

環境にやさしいオプティカルガスセンサ素子の開発 (第4報:テトラフェニルポルフィリン($TPPH_2$)誘導体を種々の生分解性ポリマーに分散した複合膜による光学的HCIガスの検出)

帆谷依美[*1]、佐々木勇生[*1]、中川克彦[*1]、堤　主計[*1]、間淵通昭[*1]、早瀬伸樹[*1]、定岡芳彦[*2]

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第33回複素環化学討論会(徳島市)、平成14年12月4日

我々は、これまでに環境汚染物質であるHCIガスをサブ-ppmレベルで検出するためのオプティカルガスセンサ用素子材の開発を行っている。本研究では、ポリマー・マトリックスとして環境共生型である生分解性ポリマーに5､10､15､20-テトラフェニルポルフイリン($TPPR_2$)誘導体を分散した複合膜をセンサ素子材に用い、HC1ガスに対する感度・応答速度等のセ：ンサ特性に及ぼすTPPRの置換基効果およびポリマー・マトリックス効果については、ビニル系ポリマーと比較検討すると共に、センサ素子材の酵素による生分解性についても検討したので報告する。

環境にやさしいオプティカルガスセンサ素子の開発(5) (第5報:テトラフエg.ルポルフィリン ($TPPH_2$) 誘導体を種々の生分解性ポリマーに分散したセンサ素子の微生物による分解特性)

帆谷依美[*1]、佐々木勇生[*1]、中川克彦[*1]、堤　計主[*1]、間淵通昭[*1]、早瀬神樹[*1]、定岡芳彦[*2]

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第33回視素環化学討論会(徳島市)、平成14年12月４日

我々は、これまでに環境汚染物質であるHC1ガスをサブ-ppmレベルで検出するためのオプティカルガスセンサ用素子材の開発を行っている。本研究では、ポリマー・マトリックスとして環境共生型である生分解性ポリマーに5,10,15,20-テトラフェニルポルフィリン($TPPH_2$)誘導体を分散した複合膜をセンサ素子材に用い、その微生物分解性に及ぼすポリマー・マトリックス効果、$TPPH_2$誘導体の置換基効果等について検討したので報告する。

lnhibition of larval barnacle attachment on the polymer film produced by marine bacterium

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7th World Conference on Biodegradable Polymers &Plastics, Tirrenia(Pisa), Italy June 4-8, 2002

Strain SHY1-1 was isolated as the polymer film-producing bacterium from Biojllys®. Strain SHY1-1 was assigned to be *Alteromonas* sp. by the physiological characteristics and 16S rRNA gene sequence. Naturally occurring Biojllys® and the polymer film produced by strain SHY1-1 were characterized by FT-IR and TLC. These results strongly suggest that the two polymeric materials would be most probably the same and a sort of mucopolysaccharide consisting of amino sugar. Anti-fouling activity of these polymers was determined by the attachment of barnacle larvae. The result indicated Biojelly® and the polymer film both had an anti-fouling activity with almost the sam6 efficiency. From these results, the polymer films produced by strain SHY1-1 are most probably the same with Biojelly®. The biodegradability of the polymer film was evaluated by incubation with or without the sea soils. The degradation of the polymer film was stimulated by the presence of sea soils. We will discuss the structure and function of these polymeric materials more in detail.

Polymer film produced by marine bacterium, *Alteromonas* sp. SHY1-1

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International Conference on ADVANCES OF BIOMATERIALS FOR RECONSTRUCTIVE MEDICINE, Capri, Italy, June 9-14, 2002

Recently, Nippon Paint Company found a polymer film(Biojelly®)that is formed on the membrane immersed in seawater. They found also that the attachment of marine organisms such as algae and barnacles decreases on Biojelly®. This phenomenon indicates that Biojelly® has anti-fouling activity. We could successfully isolate several marine microorganisms from Biojelly®.One of these isolates coded as strain SHY1-1 produced water-insoluble polymeric materials in natural seawater supplemented with yeast extracts and glucose. In order to investigate the chemical structure of naturally occurring Biojelly® and the polymer film produced by strain SHY1-1, these polymeric materials were analyzed by FTIR and TLC. These results indicated that these polymeric materials were mucopolysaccharides consisting of amino sugars. In addition, the attachment assay with larvae indicated that Biojelly® and the polymer film both had similar anti-fouling activity against barnacle (*Balanus amphitrite*).

A unique polysaccharide hydrogel secreted from marine bacterium and its antifouling activity

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Very recently, we found interesting marine bacteria which produce polymer film (registered as Biojelly®) in seawater. On the surface of Biojelly®, attachment of marine organisms such as algae and barnacles was effectively prohibited This means that Biojelly® has anti-fouling activity, One of several marine microorganisms (coded as strain SHY1-1) was isolated and assigned to be *Alterromonas* sp. by the method of the 16S rRNA gene cloning and subsequent analysis. As expected, this strain also produced water-insoluble polymeric materials in natural seawater supplemented with yeast extracts and glucose, In this work, the chemical structure and function of both naturally occurring Biojelly® and the polymer film produced by strain SHY1-1 were investigated. Results obtained indicated that these polymeric materials were a sort of mucopolysaccharide consisting of amino sugars. In addition, the attachment assay with larvae indicated that both showed anti-fouling activity against barnacle (*Balanus Amphitrite*). They were also biodegradable as expected,.

Surfaces of materials are easily covered with fouling organisms such as algae, tunicates and barnacles in seawater. Macrofouling by marine organisms is worldwide problem both economically and environmentally. Biojelly® is certainly biodegradable and shows anti-fouling activity. In this sense, Biojelly® seems rather promising for developing a new kind of ship paint.

The Enzymatic Degradation of Commercial Biodegradable Polymers by Some Lipases and Chemical Degradation of Them

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7th World Conference on BIODEGRADABLE POLYMERS&PLASTICS; June 4-8, 2002; p 128
[Grand Hotel Continental, Tirrenia(Pisa), Italy]

Polymers universally used such as PE, PP and PS have caused serious environmental pollution to be little degraded in the natural environment. To solve above problem, biodegradable polymers degraded under soil, compost, pond and sea have been developed and various commercial biodegradable polymers have been produced in some chemical companies. It has been reported that the biodegradable polyester, BIONOLLE, was degraded in activated sludge, soil and compost. In this work, five kinds of commercial biodegradable polyesters, such as poly(butylene succinate adipate)(BIONOLLE 3001), poly(butylene succinate)(BIONOLLE 1001), poly(ethylene succinate)(LUNARE SE), poly(butylene succinate)/poly(caprolactone)blend (CELGREEN HB02B)and poly(butylene adipate terephthalate)(ECO FLEX)were evaluated for enzymatic degradation by some lipases and chemical degradation in sodium hydrate solution

The enzymatic degradation of these polyesters by eleven kinds of lipases (enzyme concentration of 5 U/mg polymer)were carried out in a phosphate buffer (pH7.0)at 37°C. From the results of enzymatic degradation tests, BIONOLLE 3001, 1001 and CELGREEN HB02B were apparently degraded by lipase PS which was the most remarkably degraded polyesters among used lipases, the degradation rate was increased in the order of BIONOLLE 3001 (3.9%)> CELGREEN HB02B (44.4%)> BIONOLLE 1001 (85.9%) at 240h. For the most degraded BIONOLLE 3001 by lipase PS, the composition of polyester after enzymatic degradation for 220 h resulted in the decrease in adipate unit and the increase in succinate unit by using ^{1}H-NMR, respectively. In chemical degradation by 1N NaOH, LUNARE SE which containing short methylene unit was the most remarkably degraded among biodegradable polyesters and disappeared completely at 37°C for 20 h. In addition, ECO FLEX containing aromatics was most slowly degraded, remaining w6ight of that after 240 h was 78.6%。

Above described results lead to a conclusion that BIONOLLE 3001, 1001 and CELGREEN HB02B having relatively longer methylene unit such as butylene and pentylene unit were easy to degrade by lipase PS, on the other hand, LUNARE SE having high content of ethylene unit in polymer Chain was easily hydrolyzed in sodium hydrate solution