〔 高度技術教育研究センター 〕

〔 区 分 A 〕

中山　享

Synthesis of blue fluorescent ZrO_2:Ti,P/Al_2O_3 composite sintered bodies

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Blue fluorescence phosphor ZrO_2:Ti, P/Al_2O_3 composite bodies were fabricated by sintering {ZrO_2 + 1000 ppm Ti + 4000 ppm P} powder, which had been heat-treated at 1500° C, and α-Al_2O_3 powder at 1500° C. No cracks were observed on the fabricated blue fluorescent ZrO_2:Ti, P/10, 30, 50, and 70 wt%Al_2O_3 composite sintered bodies. The fluorescence intensities of the ZrO_2:Ti, P/10, 30, 50, and 70 wt%Al_2O_3 composite sintered bodies were 77, 82, 85 and 82%that of the ZrO_2:Ti, P blue phosphor powder, respectively. The internal quantum efficiency of the blue fluorescent ZrO_2:Ti, P/50 wt%Al_2O_3 composite bodies was 57% when excited at 280 nm..

中山　享

Synthesis of thallium silicate glasses from Tl_2O_3 and SiO_2 and their electrical properties

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Journal of the Ceramic Society of Japan, Vol.124, p.1188-1190, 2016.
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Glasses with the batch composition $(Tl_2O_3)_x(SiO_2)_{1-x}$ (x = 0.20-0.40) were synthesized by melting a mixture of Tl_2O_3 and SiO_2, and their electrical properties were investigated. It was confirmed that the Tl in the thallium silicate glasses existed in the mono- and trivalent states. The electrical conductivity of the $(Tl_2O_3)_x(SiO_2)_{1-x}$ glasses increased with an increase in the x value in the range of x = 0.20-0.40. The electrical conductivity of the glass with the batch composition of $(Tl_2O_3)_{0.40}(SiO_2)_{0.60}$ (analyzed composition: $(Tl^{1+}{}_2O)_{0.332}(Tl^{3+}{}_2O_3)_{0.061}(SiO_2)_{0.607}$) was 5.0×10^{-6}, 2.4×10^{-5}, and 9.6×10^{-5} S·cm^{-1} at 150, 200 and 250 ℃, respectively.

中山　享

High oxidation activity of thallium oxide for carbon combustion

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Thermochimica Acta, Vol.647, p.81-85, 2017.

(http://dx.doi.org/10.1016/j.tca.2016.12.005)

The catalytic behavior of thallium (III) oxide (Tl_2O_3) with respect to the combustion of carbon black was investigated using thermal analysis, X-ray diffraction analysis, scanning electron microscopy, and the ^{18}O-isotope exchange technique. The thermogravimetric-differential thermal analysis results revealed that the combustion temperature of carbon black (650 ° C) decreases dramatically, to 320 ° C, when it is mixed with Tl_2O_3 (2 wt% carbon black + as-purchased Tl_2O_3), owing to its oxidation by Tl_2O_3, which has the ability to readily release its lattice oxygens.

中山　享

Carbon oxidation characteristics of yttrium manganate catalyst prepared via urea decomposition

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$YMnO_3$ is a hexagonal crystal characterized by high carbon oxidation activity. In this study, carbon black powder has been directly oxidized at temperatures as low as 250 ° C with the active oxygen species generated by $YMnO_3$ catalyst. The activation energies measured for the non-catalyzed and $YMnO_3$-catalyzed carbon oxidation reactions were 160 $kJ \cdot mol^{-1}$ and 131 $kJ \cdot mol^{-1}$, respectively. During combustion testing of particulate matter in a ceramic form coated with $YMnO_3$, the captured soot was continuously purified at a temperature of 350 ° C.

中山　享

Preparation and luminescence of a new violet blue phosphor derived from proton-type zirconium phosphate

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Journal of Materials Research and Technology, Vol.6, p.169-172, 2017.

(http://dx.doi.org/10.1016/j.jmrt.2017.03.001)

A violet blue phosphor was prepared by thermal treatment of $HZr_2(PO_4)_3$ at 700 ° C in a reducing atmosphere and its PL was investigated. The phosphor shows violet blue emissions at around 392 nm when excited by 254 nm UV light. Its absorptivity, internal and external quantum efficiency are found to be 43, 41, and 18 %, respectively, at room temperature when excited at 254 nm. Analyses using non-dispersive infrared absorption, X-ray fluorescence, scanning electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction suggest that such an

emission originates from the formation of hydrogen and oxygen vacancies in the phosphor during the thermal treatment of $HZr_2(PO_4)_3$.

堤　主計

Effects of supercritical carbon dioxide treatment on the morphology of poly(L-lactide)

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Journal of Applied Polymer Science, Vol.133, Issue 39, p.9544-9552, (2016)

Synthetic L-lactide random copolymers can be employed as controlled release materials when prepared using supercritical carbon dioxide ($scCO_2$), since they are biodegradable via hydrolysis. To determine the effects of thermal properties on polymer performance following $scCO_2$ processing, three types of poly(L-lactide) having different properties were assessed. The T_m of one poly(L-lactide) sample (H-100) was found to be approximately 170 °C over the processing pressure range from 8 to 18 MPa, while a second sample (H-440) also showed a constant value of approximately 152 °C. In contrast, the poly(L-lactide) REVODE exhibited a T_m of 146 °C prior to processing but a higher value of 147 °C following treatment at 8 MPa. Unlike the H-100 and H-440, the T_m value of the REVODE tended to decrease with increasing pressure. The T_g values increased greatly under mild conditions of 8 MPa pressure and a temperature of 40 °C. In particular, the T_g values for the H-440 and REVODE increased by 4 °C and 5 °C, respectively. All T_g values were lowest at 12 MPa and increased with increasing processing pressure, although the effect of processing temperature was minimal. The $X_{c\ DSC}$ of the H-100 was 18% initially but increased to 20% upon $scCO_2$ processing at 40 °C and 14 MPa, and showed further increases at higher processing temperatures. Although the relationship between processing temperature and $X_{c\ DSC}$ values for the H-440 showed the same trend as observed with the H-100, a different trend was seen for the REVODE. The $X_{c\ XRD}$ values obtained from the XRD analyses differed from the values generated by DSC analysis, and showed a maximum degree of crystallinity following processing at 80 °C both with and without $scCO_2$ treatment. ATR FT-IR analyses identified peaks due to semicrystalline regions in poly(L-lactide) samples treated with $scCO_2$, even when applying low temperatures.

堤　主計

Enzymatic degradation of poly(L-lactide) treated with supercritical carbon dioxide

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Polymer Degradation and Stability, Vol.134, p.366-375, (2016)

To investigate the factors that affect the physical properties of poly(L-lactide) [poly(L-LA)] processed with supercritical carbon dioxide ($scCO_2$), the present work assessed the degradability of poly(L-LA), as well as its thermal and mechanical properties before and after

processing. The thermal properties of three types of poly(L-LA) (H100, H440 and REVODE), each having different properties, were examined. Poly(L-LA) films were treated with $scCO_2$ using a high pressure reaction apparatus at 40 ^{o}C and 14 MPa for 3 h. The treated samples subsequently underwent enzymatic degradation tests using proteinase K. The poly(L-LA)s processed with $scCO_2$ degraded more slowly compared to polymers not treated with $scCO_2$ during the early stages of degradation. Scanning electron microscopy images of the degraded, $scCO_2$-processed poly(L-LA)s indicated close spacing of the cavities generated by degradation. The T_m values of all poly(L-LA)s increased with $scCO_2$ processing, which influenced the degradability. Although the degradation of processed poly(L-LA) was slower than that of unprocessed poly(L-LA) in the early stages, the degradability of the treated H440 and REVODE samples was identical to that of specimens without $scCO_2$ processing after 160 h. In addition, the poly(L-LA) treated with $scCO_2$ was found to be degraded by proteinase K at a constant rate. The relationship between degradability and crystallinity was examined, and untreated H100 was observed to rapidly degrade in contact with proteinase K. The crystallinity indicators $X_{c\ DSC}$ and $X_{c\ XRD}$ increased after $scCO_2$ processing, such that the degradability of the treated sample was reduced. In addition, both the $X_{c\ DSC}$ and $X_{c\ XRD}$ values of untreated and treated H100 increased with degradation. Although the degradation curve of the REVODE was similar to that of the H440, the changes in the crystallinity of untreated REVODE were different from the results observed for the H100 and H440. XRD data showed that the diffraction peaks of the untreated H100 and the poly(L-LA)s treated with $scCO_2$, which were more highly crystalline, shifted to smaller angles as the enzymatic degradation progressed. Examination of the mechanical properties indicated increases in tensile strength and elastic modulus and decreases in elongation after $scCO_2$ processing, suggesting that the polymer chains were moved closer together. In conclusion, $scCO_2$ processing appears to uniformly contract polymer chains in both the amorphous and crystalline regions.

堤　主計

Carbon oxidation characteristics of yttrium manganate catalyst prepared via urea decomposition

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Ceramics International, Vol.43, p.8538-8542, (2017)

概要は前掲

〔 区　分　C 〕

中山　享

層状構造リン酸ジルコニウム中へのアルカリ土類金属の固定化（その 1）
－$ZrCa(PO_4)_2 \cdot nH_2O$ の調製－

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工業高等専門学校ものづくり教育支援センター、*4 新居浜工業高等専門学校環境材料工学科、*5 第一稀元素化学工業㈱
新居浜工業高等専門学校紀要、第 53 巻、p. 1-5、2017.

層状構造を持つリン酸ジルコニウム α-$Zr(HPO_4)_2 \cdot H_2O$ と γ-$Zr(HPO_4)_2 \cdot 2H_2O$ を中へのアルカリ土類金属の固定化について検討を行った。さらに、アルカリ土類金属として Ca を選び、層状構造を維持した $ZrCa(PO_4)_2 \cdot nH_2O$ が調製を試みた。α 型と γ 型とでは水和数の違いから Ca 置換特性の差がみられ、γ 型が Ca 置換特性に優れていた。酢酸 Ca 塩と硝酸 Ca 塩を溶かしたイオン置換用水溶液と γ-$Zr(HPO_4)_2 \cdot 2H_2O$ を反応させた結果、同温度・同反応時間では酢酸 Ca 水溶液で良好な Ca 置換特性が確認された。

堤　主計

超臨界二酸化炭素処理におけるポリエステルの機械的特性への影響

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新居浜工業高等専門学校紀要, 第 53 巻, p.13-17, (2017.1)

本研究室では、環境適応型分解性ポリエステルに揮発性化合物を含浸させる溶媒として超臨界二酸化炭素（$scCO_2$）を用いた徐放性材料の研究を行っている。$scCO_2$がポリエステルの物性に及ぼす影響を調べるために、所定の圧力や温度で処理した後、機械的特性を測定し、圧力や温度に対する影響を調べた。また、$scCO_2$は圧力や温度により密度が大きく異なるため、その影響についても調査した。本研究では、ポリエステルの構造や熱的特性の異なるポリエチレンサクシネート（PES)、ポリブチレンサクシネート（PBS）を用いた。

〔 区　分　E 〕

中川　克彦

NMR によるシイタケ生理活性成分の抽出法の影響について

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*新居浜高専専, ** (株)大愛
2017 年度日本農芸化学会大会　平成 29 年 3 月

NMR は、シイタケからの抽出成分を分離せずに非破壊的に測定を行い、スペクトル再現性が高く、試料溶液の回収ができる。本研究では、NMR 法の長所を活かし、シイタケの生理活性成分を解析し、他の分析法として LC-qTof/MS と比較検討し、シイタケ中の生理活性成分が最も高い抽出方法について報告した。

中川　克彦

シイタケ含有生理活性物質抽出法の検討(2)

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日本化学会中国四国支部大会(2016)　平成 28 年 11 月

近年、菌床栽培によるシイタケが盛んに行われている。本研究では、シイタケ栽培条件の違いまたは、乾燥シイタケの抽出法の違いによる生理活性物質（血漿コレステロール低下作用など)、Eritadenine の含有量を UV、NMR、LC-qTof により算出し、比較検討した。

中山　享

層状構造リン酸ジルコニウム中へのアルカリ土類金属の固定化

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第 23 回　ヤングセラミスト・ミーティング in 中四国
2016 年

水溶液中において、二次元層状構造 $Zr(HPO_4)_2 \cdot nH_2O$ 中の H^+ を 2 価のアルカリ土類金属元素（M^{II}）とイオン置換（固定化）する方法により層状構造 $ZrM^{II}(PO_4)_2 \cdot nH_2O$ の作製を検討した。

堤　主計

生分解性プラスチックを用いた環境適応型徐放剤

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平成 28 年度愛媛農林水産業スゴ技マッチング交流会
2016 年 9 月

開発した“徐放剤”は、基材に①土壌中や水中で分解されやすく環境にやさしいことでよく知られている生分解性プラスチックを用い、その中に②天然に存在する有用な薬剤（揮発性物質）を超臨界二酸化炭素（$scCO_2$）により含浸させた新しい材料である。揮発性の高い物質をプラスチック中に含浸させることは従来技術では非常に難しかったが、$scCO_2$中で処理することにより簡単に含浸させることに成功した。生分解性プラスチックは土壌に存在する微生物や水（湿気）によって簡単に分解されるという性質があり、今回開発した徐放剤でも同じように基材に用いた生分解性プラスチックが分解し、それに伴い含浸させていた揮発性物質が長期間にわたりゆっくりと放出され、薬効を持続させることができる。また、加工処理で基材は変形することがないため、様々な形態に対応することができる。

堤　主計

超臨界二酸化炭素処理によるポリ乳酸のモルフォロジーに関する研究

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第 65 回高分子討論会
2016 年 9 月

二酸化炭素は、臨界温度 31.1℃・臨界圧力 7.38 MPa 以上で超臨界状態となり、超臨界二酸化炭素($scCO_2$)は安全性に優れ、反応後に気体として容易に除去できるため、医療用マイクロカプセルの調整やポリマーへの薬剤の均一な分散などに利用されている。また、$scCO_2$は疎水性の媒体で、低い温度で超臨界状態であるため、熱的特性の低い生分解性ポリマーの加工媒体として利用されている。我々は $scCO_2$の処理条件によって、ポリ乳酸などの生分解性ポリマーへの忌避薬剤などの精油の含浸量が異なることを報告したが、その含浸メカニズムは明らかになっていない。薬剤の含浸は $scCO_2$におけるポリマーのモルフォロジー変化も要因の一つとして考えられるため、$scCO_2$処理後のポリ乳酸の各種物性値を測定し評価した。本研究では、$scCO_2$処理したポリ乳酸の DSC 測定による熱的特性の変化や XRD や ATR FT-IR 測定により分子構造の変化を評価した。$scCO_2$処理による物性変化を特徴付けるために、熱処理したポリ乳酸の各種測定を行い、そ

の違いを評価した。

松原　靖廣

超臨界二酸化炭素処理によるポリ乳酸のモルフォロジーに関する研究

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概要は前掲