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Heat-ray Shielding Property of Nanocomposites of Poly(acrylic acid) Doped with Copper Sulfide

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Abstract

The aim of our study is to prepare nanocomposites consisting polymer/inorganic nanoparticles and investigate their physical properties as a functional material. In this study, a nanocomposite of copper sulfide (CuS) nanoparticles introduced into a poly(acrylic acid) matrix was prepared and the optical absorption property was measured. The composite exhibited strong absorption of both ultraviolet and near-infrared rays, indicating that the composite is applicable to a solar radiation shielding filter. The wavelength of the near infrared absorption was controlled from ca.1000 nm to 1700 nm by heat and acidic solution treatments.

Introduction

Organic/inorganic composite materials consisting of polymers doped with metal or semiconductor nanoparticles, which possess characteristic optical properties, such as optical absorption, non-linear optical, and laser amplification properties, have recently attracted increasing interest for potential application as novel photonics devices. In contrast to inorganic matrices such as glasses or ceramics, the use of organic polymers as a matrix has the advantages of processability and ease of handling of the composite materials. Specifically, the polymer matrices can be molded at lower temperature, and show generally higher flexibility and toughness than inorganic matrices. Furthermore, various inorganic compounds for doping components can be readily introduced in the polymer matrices using *in-situ* reactions under mild conditions.

Heat-ray shielding materials are required in architectural glazing to reduce the heating of building interior under solar radiation in hot weather. In particular, blocking infrared ray properties are desirable to save energy during air conditioner use in buildings or cars.

Some copper compounds exhibit near-infrared absorption useful for solar radiation shielding materials [1-4]. Copper sulfide, a *p*-type semiconductor has been frequently investigated due to its attractive optical and electrical properties.

In this study the author reports the preparation of nanocomposite materials of Poly(acrylic acid) (PAA) doped with copper sulfide particles using *in-situ* precipitation in a polymer matrix, and the near-infrared absorption property and structures of the composites were investigated in terms of application as a heat-ray shielding material.

Experimental

Crosslinked PAA films (thickness: ca. 20 μm) were prepared by bulk-coplymerization of 85 mol% acrylic acid and 15 mol% triethylen glycol dimethacrylate by UV irradiation. The copper salt of PAA was prepared by immersing the PAA film in 2 wt% copper(II) acetate aqueous solution for 2 hours, and then the Cu^{2+} component in the film was sulfurized by immersing in 10 wt% $Na_2S \cdot 9H_2O$ aqueous solution for 2 hours. After sulfuration a dark yellow transparent composite film was obtained. The composite film is represented by PAA-CuS.

Results and Discussion

From TEM and small angle X-ray scattering measurements, spherical particles having the diameter of ca. 5-6 nm were found to disperse in a PAA-CuS film. The particles were confirmed as CuS by wide angle X-ray diffraction and elemental analysis. Fig.1a and 1b show the ultraviolet-visible-near infrared (UV-VIS-NIR) absorption spectra for the PAA-CuS films annealed at various temperatures for 2 min, and treated in 0.1 mol% HCl solution at different treatment times, respectively. In the figures, the temperature and time shows an annealing temperature and treatment time, respectively. For the untreated sample, the composite film strongly absorbed both UV and NIR rays due to optical absorption of the copper sulfide nanoparticles. Copper sulfide is known as a *p*-type semiconductor which has relatively large electrical conduction. The absorption of UV ray is due to interband transition, while the absorption of NIR ray is attributed to plasma oscillation by free carriers. The absorption wavelength by plasma oscillation can be changed depending on the density of free carrier based on the following equation [5]:

$$\nu_p = (1/2\pi)\sqrt{Nq^2/\varepsilon_0 m^*}$$

where ν_p, N, q, ε_0, and m^* are plasma frequency, electron density, electron charge, permittivity of vacuum, and effective mass, respectively. That is, the wavelength of plasma oscillation by CuS is in inverse proportion to $N^{1/2}$. In the case of electrical conducting CuS, N is considered the density of positive hole as a free carrier.

The wavelength of absorption maximum centered at 1250nm of the composite could be varied by annealing at 200 - 280 °C. The wavelength of the peak maximum increased with increase of annealing temperature. This implies that annealing above 200 °C reduces the N value and leads to the shift of the absorption to the longer wavelength side. Decrease of N should be accompanied by the decrease of absorbance, because the number of free carrier which absorbs NIR ray decreases.

In contrast to the annealing, the wavelength of absorption maximum shifts to shorter wavelength side by the acidic treatment in HCl aqueous solution. Within ca. 1 hour of the treatment time, the wavelength of the peak maximum increased and the absorbance decreased with increase of the treatment time. The mechanism of the changes of N by the treatments is unknown in detail, which are currently being studied.

This result indicates that the composite film is useful as a solar radiation shielding material. In actual, the PAA-CuS film prevented from heating up the temperature in a thermally insulated box exposed by a heat lamp.

Conclusion

The wavelength of the near infrared absorption was controlled from ca.1000 nm to 1700 nm by heat and acidic solution treatments. This result indicates that the composite film is useful as a heat-ray shielding material.

References

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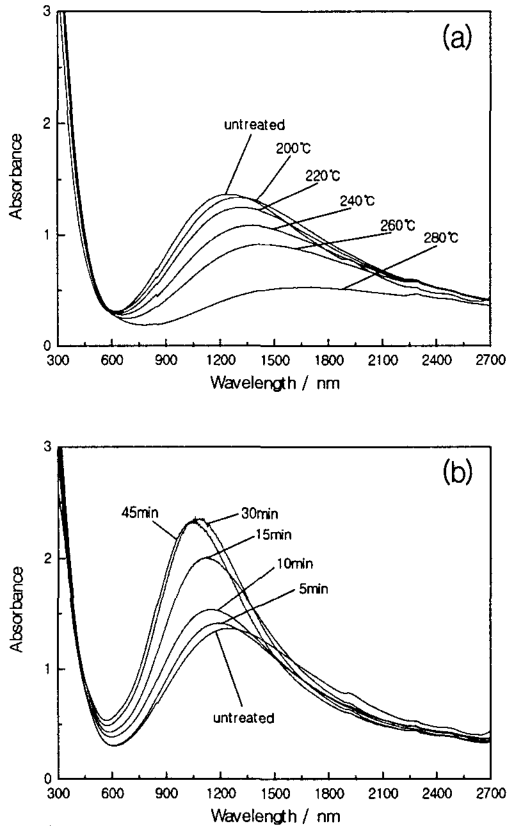

Fig.1 UV-VIS-NIR spectra for the PAA-CuS films annealed at various temperatures (a) and treated in 0.1 mol% HCl solution at different treatment times (b).